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Dual Alkali Test and Evaluation Program Volume III. Prototype Test Program - Plant Scholz

Arthur D. Little, Inc, Cambridge, Mass

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FINAL REPORT: DUAL ALKALI TEST AND EVALUATION PROGRAM
Volume III. Prototype Test Program—Plant Scholz

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Program Report

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ABSTRACT

This report presents the results of the Dual Alkali Program conducted by Arthur D. Little, Inc. (ADL) for the Industrial Environmental Research Laboratory, Research Triangle Park, (IERL, RTP) of the U.S. Environmental Protection Agency (EPA). The purpose of the program was to investigate, characterize and evaluate the basic process chemistry and the various modes of operation of sodium-based dual alkali processes. The work was carried out at three levels of investigation:

- Task I - Laboratory studies at ADL and IERL, RTP.
- Task II - Pilot Plant Operations in a 1,200 scfm system at ADL.
- Task III - Prototype Test Program on a 20-megawatt Combustion Equipment Associates (CEA)/ ADL dual alkali system at Plant Scholz, Southern Company Services, Inc./Gulf Power Company.

Various modes of operating dual alkali systems on high- and low-sulfur fuel applications were investigated, including:

- Concentrated and dilute sodium scrubbing systems
- Lime and limestone regeneration
- Slipstream sulfate treatment schemes.

In each mode, the objective was to characterize the dual alkali process in terms of SO_2 removal, chemical consumption, oxidation, sulfate precipitation and control, waste solids characteristics and soluble solids losses.

This is Volume III of the final report covering the Prototype Test Program, Task III. Volume I is the Executive Summary; Volume II covers Tasks I and II, the Laboratory and Pilot Plant Programs.

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VOLUME III

TASK III, PROTOTYPE TEST PROGRAM

TABLE OF CONTENTS

Chapter		Page No.
	LIST OF FIGURES	ix
	LIST OF TABLES	x
	ABSTRACT	iii
	ACKNOWLEDGEMENTS	xiii
	APPLICABLE CONVERSION FACTORS ENGLISH TO METRIC UNITS	xv
I	SUMMARY	I-1
	A. PURPOSE AND SCOPE	I-1
	B. PROGRAM DESCRIPTION	I-2
	1. System Design	I-2
	2. System Operation	I-2
	C. SYSTEM PERFORMANCE	I-3
	1. SO_2 Removal	I-3
	2. Particulate Removal	I-4
	3. Lime Utilization	I-4
	4. Oxidation/Sulfate Control	I-4
	5. Waste Cake Properties	I-6
	6. Sodium Makeup	I-7
	7. Power Consumption	I-7
	8. Operability/Reliability Potential	I-7
II	INTRODUCTION	II-1
III	SYSTEM DESCRIPTION	III-1
	A. PROCESS CHEMISTRY	III-1
	B. SYSTEM CONFIGURATION	III-2
	1. Flue Gas Scrubbing	III-5
	2. Absorbent Regeneration	III-8
	3. Solid/Liquid Separation and Solids Dewatering	III-10

Preceding page blank

TABLE OF CONTENTS (cont)

Chapter		Page No.
IV	OPERATING HISTORY	IV-1
	A. GENERAL OPERATING CONDITIONS	IV-1
	B. DESCRIPTION OF OPERATING PERIODS	IV-1
	1. Operating Period 1 -- Startup and Initial Operations	IV-1
	2. Operating Period 2 -- Low- to Medium-Sulfur Coal Operation	IV-5
	3. Operating Period 3 -- High-Sulfur Coal Operation	IV-7
V	SYSTEM PERFORMANCE	V-1
	A. AVAILABILITY	V-1
	B. PROCESS PERFORMANCE -- STABLE LOAD OPERATION	V-2
	1. Overall Operation	V-2
	2. SO_2 Removal	V-10
	3. Lime Utilization	V-15
	4. Oxidation and Sulfate Control	V-17
	5. Waste Cake Properties	V-25
	6. Sodium Makeup	V-31
	7. Process Operability	V-33
	C. PROCESS PERFORMANCE -- FLUCTUATING LOAD	V-35
	1. SO_2 Removal	V-39
	2. System Chemistry (Sulfite Oxidation)	V-39
	3. Lime Utilization	V-39
	4. Waste Solids Properties	V-40
	5. System Operability	V-40
	D. PROCESS PERFORMANCE -- PARTICULATE TESTING	V-40
	1. Particulate Removal	V-43
	2. SO_2 Removal	V-48

TABLE OF CONTENTS (cont)

Chapter			Page No.
V (cont)		3. Chloride Removal	V-48
		4. Lime Utilisation	V-48
		5. System Chemistry (Oxidation and Sulfate Control)	V-49
		6. Waste Cake Properties	V-49
		7. Liquor Entrainment	V-50
		8. Overall Operability	V-50
	E.	MECHANICAL PERFORMANCE	V-50
		1. Equipment	V-52
		2. Instrumentation	V-56
VI	REFERENCES		VI-1
VII	GLOSSARY		VII-1
	APPENDICES		
	Appendix A - Daily Coal Analyses		A-1
	Appendix B - Process and Boiler Outages		B-1
	Appendix C - Process Operating Data		C-1
	Appendix D - Typical Process Flows and Stream Compositions		D-1
	Appendix E - Solution Composition/pH Correlations		E-1
	Appendix F - Scrubber System Efficiency Estimates		F-1
	Appendix G - Equipment Problems		G-1

VOLUME III

LIST OF FIGURES

Figure No.		Page No.
III-1	CEA/ADL Dual Alkali System at the Scholz Steam Plant - Process Flow Diagram	III-4
III-2	Gas Scrubbing System	III-6
III-3	Absorbent Regeneration and Chemical Makeup System	III-9
III-4	Solids Dewatering System	III-11
V-1	Availability of the CEA/ADL Dual Alkali System at Scholz	VI-3
V-2	SO_2 Removal as a Function of pH - Low/Medium-Sulfur Coal	V-11
V-3	SO_2 Removal as a Function of pH - High-Sulfur Coal	V-12
V-4	Oxidation in the Scrubber System as a Function of Flue Gas Oxygen Content (Periods 1 and 2)	V-19
V-5	Oxidation in the Scrubber System as a Function of Flue Gas Oxygen Content (Period 3)	V-20
V-6	($CaSO_4/CaSO_3$) Ratio in Waste Solids as a Function of (Na_2SO_4/Na_2SO_3) Ratio in Regenerated Liquor	V-22
V-7	Filter Station - Showing Filter Cake in Storage/Transfer Bin Below Filter	V-26
V-8	Loading Filter Cake for Transport to Disposal Pond	V-27
V-9	Gas Load Schedule for Fluctuating Load Testing	V-36
V-10	Schematic of the Electrostatic Precipitator on Boiler #1 at Scholz Steam Plant	V-41
V-11	Schedule of Precipitator Operation and Scrubber Tests	V-44
V-12	Liquor Entrainment vs Gas Flow Measured by York Research (6/76)	V-51

Preceding page blank

VOLUME III

LIST OF TABLES

Table No.		Page No.
III-1	Design Basis	III-1
IV-1	Summary of Operating Periods	IV-2
IV-2	Summary of System Inlet Conditions - Operating Period 1 (2/75-7/75)	IV-4
IV-3	Summary of System Inlet Conditions - Operating Period 2 (9/75-1/76)	IV-6
IV-4	Summary of System Inlet Conditions - Operating Period 3 (3/76-7/76)	IV-8
V-1	Summary of Prototype System Availability	V-4
V-2	Summary of System Operating Conditions - Period 1 (3/75-6/75)	V-5
V-3	Summary of System Operating Conditions - Period 2 (10/75-12/75)	V-6
V-4	Summary of System Operating Conditions - Period 3, Stable Load Testing (4/76-5/76)	V-7
V-5	Summary of Overall System Performance During Stable Load Testing (4/75-6/76)	V-9
V-6	SO_2 Removal Performance During Stable Load Operation	V-14
V-7	Lime Utilization During Stable Load Operation	V-16
V-8	System Sulfate Balances	V-24
V-9	Summary of Filter Cake Properties	V-28
V-10	Summary of System Operating Conditions Fluctuating Load Testing	V-37
V-11	Comparative Performance Characteristics Stable vs Fluctuating Load	V-38

LIST OF TABLES (cont)

Table No.		Page No.
V-12	Summary of System Operating Conditions Particulate Testing (6/15-7/1/76)	V-44
V-13	Summary of Scrubber Test Conditions	V-45
V-14	Summary of System Performance	V-46
V-15	Summary of Particulate Test Results	V-47

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APPLICABLE CONVERSION FACTORS

ENGLISH TO METRIC UNITS

British	Metric
5/9 (°F-32)	°C
1 ft	0.3048 meter
1 ft^2	0.0929 $meters^2$
1 ft^3	0.0283 $meters^3$
1 grain	0.0648 gram
1 in.	2.54 centimeters
1 in^2	6.452 $centimeters^2$
1 in^3	16.39 $centimeters^3$
1 lb (avoir.)	0.4536 kilogram
1 ton (long)	1.0160 metric tons
1 ton (short)	0.9072 metric tons
1 gal	3.7853 liters
1 Btu	252 calories

1. SUMMARY

A. PURPOSE AND SCOPE

This report presents the final results of the Dual Alkali Test Program conducted on the 20-megawatt (nominal capacity) dual alkali prototype system at Gulf Power Company's Scholz Steam Plant in Sneads, Florida. The prototype system was designed and built by Combustion Equipment Associates, Inc. (CEA) and Arthur D. Little, Inc. (ADL) for Southern Company Services, Inc. (SCS) and the Gulf Power Company. The test program represents Task III of the Dual Alkali Program conducted by ADL for the Industrial Environmental Research Laboratory (IERL) of the U.S. Environmental Protection Agency (EPA).

The purpose of the test program was to characterize and evaluate the performance of the dual alkali process operating in a concentrated active sodium mode with lime regeneration. The formal test program lasted a total of about 14 months and covered a variety of conditions, including operating with low-, medium-, and high-sulfur coal. The effects of both fluctuating gas loads and simultaneous particulate removal were also tested in conjunction with high-sulfur coal operation.

The operation of the system was evaluated with regard to the following performance characteristics used to evaluate all dual alkali modes:

- SO_2 removal efficiency;
- lime utilization;
- oxidation/sulfate control;
- waste solids properties;
- sodium makeup requirements and degree of closed-loop operations; and
- overall system operability and reliability potential.

While the overall operability and reliability were a principal concern, the system was not intended to be a demonstration unit to test the ultimate availability of such systems in full-scale applications. The test program was focused on evaluating the viability of the process technology and defining process capabilities and limitations. The process reliability and operability were, therefore, of importance primarily as they reflected process chemistry and operational problems related to process chemistry.

B. PROGRAM DESCRIPTION

1. System Design

The 30-megawatt prototype system was installed on Unit No. 1, a 40-megawatt (nominal capacity) Babcock and Wilcox pulverized-coal-fired power boiler. The boiler is equipped with a high-efficiency, sectionalized electrostatic precipitator. The system consisted of basically three process sections: scrubbing; absorbent regeneration; and waste solids dewatering. The scrubbing system contained a venturi followed by an absorption tower with two trays and a demister. The scrubber system was designed with the flexibility of operating either in a direct lime or limestone scrubbing mode as well as dual alkali. The venturi was included for testing simultaneous particulate and SO_2 removal. Modifications to the scrubber system following startup of the system provided for operation of the venturi alone by bypassing regenerated liquor around the absorber.

The regeneration system consisted of the CEA/ADL two-stage reactor system. Provisions were made for feeding dry or slurried hydrated lime to either or both reactors.

The waste solids dewatering system consisted of a thickener and a single rotary drum vacuum filter equipped with wash sprays. The thickener was sized to handle 40 megawatts of capacity in contrast to the scrubbers, reactor, and filter, which were designed for 30 megawatts.

The system was designed to operate in the concentrated active sodium mode on medium- and high-sulfur coal. In this mode, sulfate removal cannot be accomplished by precipitation of gypsum ($CaSO_4 \cdot 2H_2O$); rather, calcium sulfate is precipitated along with calcium sulfite, resulting in a mixed crystal of the two salts.

2. System Operation

The prototype system was started up on February 3, 1975 and was operated over a period of 17 months, through July 2, 1976. The EPA Test Program formally began in May 1975 and was completed in July 1976, after which the system was shut down. This report covers the entire 17 months of operation, including system startup and shakedown.

The operation of the system can be logically broken down into three discrete periods as defined by coal composition, flue gas conditions, and the characteristics of the system operation. The first period, from February through July 1975, covered system startup and shakedown. During these first six months of operation the boiler burned low-sulfur coal (average sulfur content corresponding to approximately 2.6 lb SO_2/MM Btu). Sulfur dioxide concentrations in the flue gas averaged 1,050 ppm (range = 600-1,550 ppm) and oxygen levels averaged 7.5% (range = 5.0-11.0%) -- conditions well outside the range for which the process was originally designed. This represented a difficult test for a system operating in the concentrated active sodium mode because of the levels of oxidation experienced.

In the second operating period, lasting from September 1975 through early January 1976, the system was tested under relatively stable load conditions with the boiler firing a combination of medium- and low-sulfur coals. (The average sulfur content of the coal fired corresponded to approximately 3.1 lbs SO_2/MM Btu.) During this period the electrostatic precipitator was maintained in full service. Repairs to the boiler combustion air preheater and better control of combustion resulted in improved flue gas conditions in comparison to operations in Period 1. Sulfur dioxide levels in the flue gas during Period 2 averaged 1,250 ppm (range = 800-1,700 ppm), and oxygen concentrations averaged 6.0% (range = 4.5-9.5%).

In Period 3, which lasted from March through early July 1976, the system was tested on high-sulfur coal (average sulfur content in the coal corresponding to about 5.7 lbs SO_2/MM Btu). Flue gas SO_2 levels averaged about 2,250 ppm (range = 1,500-2,800 ppm), and oxygen concentrations averaged about 6.5% (range = 4.5-9.0%).

In addition to 10 weeks of operation at relatively stable load, testing during Period 3 consisted of three weeks of operation at fluctuating gas loads and two weeks of particulate testing. The fluctuating load testing involved adjusting the gas flow to the system to four different levels according to a prearranged schedule roughly representative of the normal load swings of the Scholz boilers. The average gas rate handled during fluctuating load testing was 65%, as compared with 85-90% during the stable load periods. Particulate testing was performed during the last two weeks of the program to evaluate the effects of fly ash on the system performance (SO_2 removal, scale formation, oxidation, and waste cake properties) and to assess particulate removal efficiency and mist eliminator performance. During these two weeks the operation of the precipitator ranged from fully activated to completely deactivated.

C. SYSTEM PERFORMANCE

Overall, the performance of the system was excellent. The system demonstrated high SO_2 removal efficiency, high lime utilization, excellent waste cake properties, and very good overall availability. The various aspects of system performance are discussed below.

1. SO_2 Removal

SO_2 removal efficiencies at Scholz confirm the high SO_2 removal capability of sodium solution scrubbing in the concentrated active sodium mode. With sodium solution scrubbing, achieving a given outlet SO_2 level (within the limit of the number of contact stages used) is essentially a matter of adjusting the operating pH of the scrubber system (by adjusting the feed forward rate or regenerated liquor pH). Over the 15 months between April 1975 and July 1976, the average SO_2 removal using both the venturi and absorber (with two trays) was 95.5% (for low-, medium-, and high-sulfur coal); with the venturi alone (low-sulfur coal only) SO_2 removal efficiency averaged 90.7%.

For the most part, when both the venturi and absorber were operated together, the venturi was used principally for quenching the gas, and the venturi pressure drop was maintained in the range of 4.5 to 7.0 inches of water. Under these conditions the pH of the venturi bleed liquor was maintained between 4.8 and 5.9 to ensure better than 90% SO_2 removal. With the low inlet SO_2 levels of Periods 1 and 2 (600-1,700 ppm) this resulted in outlet SO_2 levels generally ranging from 15 to 100 ppm. At the higher inlet SO_2 levels of Period 3 (1,500-3,800 ppm), the outlet SO_2 typically ranged from 25 to 150 ppm.

When the venturi alone was used (10-16 inches of water pressure drop), the bleed liquor was generally maintained at a pH above 5.7 to keep outlet SO_2 levels below 100 ppm.

2. Particulate Removal

The particulate removal capability of the scrubber system was tested with the venturi operated at both 12 and 17 inches of water pressure drop followed by the absorber containing two trays. Three ranges of inlet particulate loadings were tested (by partially or wholly de-energizing the precipitator): 0.015-0.025 grains/standard cubic foot dry (grs/scfd); 0.03-0.085 grs/scfd; and 2.3-3.6 grs/scfd. In general, outlet particulate loadings increased slightly with increasing inlet loadings, as would be expected. Outlet loadings ranged from 0.010-0.015 grs/scfd at the lowest inlet loadings to 0.024-0.037 grs/scfd at the highest inlet loadings. However, there was no statistical difference in outlet loadings between operations at 12 and 17 inches of pressure drop across the venturi throat (undoubtedly due, at least in part, to the two trays). At these high venturi pressure drops, the SO_2 removal increased to an average of about 98% for the particulate test period (using high-sulfur coal).

3. Lime Utilization

Lime utilization throughout all three operating periods was quite good. Under normal conditions, lime utilization ranged from 90% to 100% of the available $Ca(OH)_2$ in the raw, hydrated lime and typically ran 93% to 97%. (The $Ca(OH)_2$ fraction of the delivered lime ranged from 87% to 91% wet basis.) There was no discernible effect of fluctuating load, simultaneous particulate removal, or manner of lime feed (dry vs. slurry) on lime utilization. Utilization during operations with high-sulfur coal, though, tended to average closer to 93%; while in operations with low-sulfur coal, it ran 96% to 97%. This slight difference has been attributed to the shorter holdup time in the reactor [illegible] at the higher feed forward rates with high-sulfur coal.

4. Oxidation/Sulfate Control

a. Oxidation

Oxidation rates experienced in the prototype system were slightly lower than those observed in the pilot plant under similar conditions. As in

the pilot operation, though, oxidation in the scrubber circuit accounted for 80-95% of oxidation throughout the system. The principal variable affecting oxidation was the oxygen content of the flue gas, although the flue gas rate and the type of coal fired also had some effect.

With the low- and medium-sulfur coals fired in Periods 1 and 2, oxidation rates in the scrubber system ranged from about 180 ppm equivalent SO_2 (~ 230 ppm in the entire system) at 5% oxygen in the flue gas to about 370 ppm equivalent SO_2 (~ 420 ppm in the entire system) at 9% oxygen in the flue gas. The total system oxidation rates correspond to a range of 30% to 45% of the SO_2 removed for the average inlet levels for these periods. However, there was considerably more gas/liquid contacting provided in the scrubber system (venturi + two trays) than would normally be incorporated in an absorption system for a low-sulfur coal application. This not only resulted in very low outlet SO_2 levels (typically less than 50 ppm) but also unnecessarily high rates of oxidation (as a percentage of SO_2 removed).

With the high-sulfur coal in Period 3, the absolute rate of oxidation in the scrubber system increased slightly. At 5% oxygen in the flue gas, oxidation in the scrubber system averaged about 200 ppm equivalent SO_2 (~ 250 ppm throughout the system); and at 9% oxygen, oxidation in the scrubber ran slightly over 300 ppm (~ 350 ppm throughout the system). These higher oxidation rates, though, represent lower percentages of oxidation in terms of SO_2 removed. For the average SO_2 removal in Period 3 these oxidation rates correspond to about 10% and 25% of the SO_2 removal, respectively.

As would be expected, the absolute rate of oxidation (mols/min) decreased with reductions in gas flow, although the percentage of SO_2 oxidized increased slightly. No effect of fly ash on oxidation was apparent during the particulate testing period.

b. Sulfate Precipitation

Precipitation of calcium sulfate measured in the reactor system showed that calcium sulfate could be coprecipitated with calcium sulfite at levels as high as 25% of the total calcium sulfur salts, indicating that the system was capable of keeping up with such levels of oxidation. The correlation of sulfate/sulfite content of the precipitated calcium salts to sulfate/sulfite concentrations in the reactor liquor was found to be:

$$\left(\frac{\text{mols } CaSO_4}{\text{mols } CaSO_3}\right)_{\text{reactor solids}} = 0.031\left(\frac{[SO_4^=]}{[SO_3^=]}\right)_{\text{reactor liquor}} \qquad (1)$$

This degree of sulfate coprecipitation corresponds to about 85% of that observed in the pilot plant.

There was also a slight decrease in the calcium sulfate/sulfite ratio in the filter cake in comparison with that in the reactor product solids. The data indicate about a 15% decrease in the sulfate content between the reactor and filter. This is probably due to some dissolution of calcium sulfate during the long holdup in the thickener.

Overall, the sulfate formation (oxidation)/sulfate precipitation data show that the system is capable of keeping up with oxidation rates of up to 25% of the SO_2 removed -- oxidation rates much higher than those anticipated for most medium- and high-sulfur coal applications. The operation at the widely fluctuating conditions demonstrated the stability of the system chemistry and its ability to "self-adjust" to handle any oxidation rate up to 25% without operator intervention. As oxidation changed, the ratio of sulfate to active sodium in the liquor changed accordingly to increase or decrease the amount of calcium sulfate precipitated.

5. Waste Cake Properties

a. Solids Content

The solids content of the waste filter cake varied from 41% to 77% of the total cake weight. In general, the solids content of the cake varied with calcium sulfate content (decreasing with increasing calcium sulfate levels) and with variations and upsets in the filter operation. During stable load conditions the average solids content of the filter cakes produced in each successive operating period increased from 48% in Period 1 (low-sulfur coal) to 54% in Period 3 (high-sulfur coal). The inclusion of fly ash during simultaneous particulate removal in Period 3 increased the average solids content to about 57%. These averages include periods of minor filter upsets and partial loss of vacuum.

Under most all conditions the cake had the appearance and handling properties of a moist soil. It was easily transferred from the storage pile to dump trucks using a front-end loader for transfer to the disposal pit.

b. Solubles Content

Wash efficiency tests performed on the prototype filter verified pilot plant results regarding the washability of the cake. The results show that the soluble solids levels in the cake can be readily reduced to 2-3% (dry cake basis) under controlled filter conditions using a wash ratio of about 2.5 (gals wash water/gal water occluded in the cake). The solubles levels actually achieved on a continuous basis, though, were higher due to the limited capacity of the spray nozzles, system upsets, and inadequate operator attention to cake washing. Soluble solids levels in the cake throughout the program ranged from as low as 1.2% to as high as 12% of the dry cake weight, depending upon the degree of washing and the solids content of the filter cake. The average losses

estimated for each operating period based upon cake analyses and overall material balances ranged from 4% (Period 3) to as high as 8% (estimated, Period 1). The average solubles losses, though, were biased upward by the fluctuating wash conditions. Long periods of adequate cake washing were more than offset by short periods of poor cake washing (due to high rates of cake withdrawal required to catch up with the single filter, and inattention to wash water rates).

6. Sodium Makeup

The rate of sodium makeup to the system in comparison to the estimated sodium value losses in the filter cake provide a measure of the degree of closed-loop operation (as well as accountability in the overall material balances). Soda ash feed rates were closely monitored only during Periods 2 and 3. During Period 2 soda ash makeup rates represented about 6% of the total SO_2 removal (mols Na_2CO_3/mol ΔSO_2) compared with about 4.5% soda ash requirements based upon cake losses. The difference is attributed to pump seal leaks, a small thickener leak that developed during Period 2, and errors in the overall material balance. Entrainment losses of sodium (in entrained liquor) were negligible. As measured in both December 1975 and June 1976, entrainment losses were equivalent to less than 0.1% of the ΔSO_2 (as soda ash required). During Period 1 the material balance on sodium was almost completely closed. The soda ash required to make up for cake losses was about 7% of the SO_2 removal (using an average wash ratio of 1.8) versus a soda ash feed rate of 6% of the SO_2 removal.

While soda ash requirements were slightly higher than desired due primarily to inadequate control of the filter operation, the relatively small soda ash requirements and the degree of closure in the soda ash material balance reflect a tight, closed-loop operation.

7. Power Consumption

Since the process included a venturi scrubber as well as additional pump capacity for operation in a direct lime or limestone mode, the power consumed in the dual alkali mode was greater than that which would be consumed in a system designed specifically as a dual alkali system. When operating at or near design gas flow, the system power consumption averaged 2.5-3.0% of the boiler output. Correcting for the additional pressure drop included with the venturi and the unnecessary pump capacity, the power consumed by the equipment actually required for this application was about 1.0% of the capacity of the boiler.

8. Operability/Reliability Potential

a. Availability

While the system was not operated for the purpose of achieving a high availability figure, the availability record of the system is impressive. Over the 17 months of operation the system logged more than 7,100 hours

of operation, which corresponded to an overall availability of slightly higher than 70%. Most of the downtime occurred between the operating periods and resulted from equipment problems of a mechanical nature or problems caused by operation of the system well outside the design conditions. The availability during the operating periods averaged about 90%. This availability is impressive, particularly in light of the fact that the only spare equipment was pumps (and replacement parts for unspared equipment were minimal), and that the system was called upon to operate about 70% of the time at conditions outside those for which it was designed.

The longest single outage (1,460 hours) occurred between Periods 1 and 2. During the end of Period 1, oxygen levels in the flue gas were running in the range of 8-10%, with inlet SO_2 levels depressed to 850-950 ppm. Because of the resulting high oxidation levels (as a percentage of SO_2 removal) the system was allowed to drift into a dilute active sodium mode, a mode for which it was not designed. The result was precipitation of gypsum and formation of some gypsum scale in the reactor tanks and piping. At the same time, mechanical problems in the scrubber required a shutdown of the system, and it was decided to await repair of the preheater and higher-sulfur coal prior to restart of the system. There was also some delay in replacement parts, so the system remained down from mid-July through mid-September 1975. Such delays would not normally be encountered in full-scale applications with adequate sparing of equipment and maintenance of a reasonable inventory of spare parts.

Between Periods 2 and 3 the boiler was shut down for scheduled maintenance. The system remained out of service an additional month following boiler startup, again due to delays in shipments of replacement parts and equipment being overhauled.

b. Equipment Performance

Most of the problems encountered with equipment and instrumentation during the course of the test program were mechanical in nature and reflected design or fabrication oversights commonly associated with a prototype system. All but a few were resolved during the course of the test program by simple operational adjustments and/or equipment modifications.

Equipment

The most significant equipment problems encountered in the system involved the filter, vessel linings, scrubber control and block valves, and solids buildup in the first-stage reactor. Collectively, these accounted for the bulk of mechanical-related downtime and maintenance.

- The filter was the largest source of problems in the prototype system, but the problems resulted in few system outages due to the solids holdup capacity in the thickener, which allowed sufficient time for most filter-related maintenance work. Normally, filters do not require an inordinate amount of maintenance.

However, a large part of the filtration equipment in the prototype system was fabricated out of fiberglass and plastic because of both anticipated corrosion problems from the high chloride levels achieved in the tight, closed-loop operation (9,500-11,000 ppm Cl^-) and to minimize the cost for the short-term prototype test program. Fiberglass is not as sturdy as stainless steel, and there were failures at stress points in the construction as well as erosion of some of the plastic and fiberglass parts. Most of the problems occurred during Period 1 and the early part of Period 2. Modifications of the filter drum and tub by plant personnel, and overhaul of the filter drum by the manufacturer between Periods 2 and 3 either eliminated the problems or reduced them to routine, low-level maintenance.

- Lining erosion or lining cracks and pinholes occurred in various vessels in the system. Cracks and pinholes occurred in the absorber recycle tank and the thickener floor and walls. These were patched during interim periods and did not reoccur during the remainder of the test program. Erosion of lining occurred beneath the agitator in the second-stage reactor vessel and on the liquor redistribution shelf in the venturi. These linings were also patched in the interim between Periods 2 and 3, and the venturi tangential nozzles modified. No further erosion at either location was observed. There was also deterioration of the lining in the area of the quench zone at the gas inlet to the venturi. The cause of the failure may have been a combination of factors including poor application, inadequate surface preparation, and severity of temperature and chemical attack. This failure suggests that corrosion-resistant metal alloys may be most suitable in such areas.

- Erosion and "debonding" of rubber linings occurred in control and block valves in the scrubber system. These failures were traced to the high degree of throttling in the control flow. (The valves were sized to accommodate the higher flows associated with direct lime slurry scrubbing.) These valves were replaced with 316 stainless steel valves prior to Period 3 and no further erosion or debonding occurred in the valves. There was also no corrosion or erosion of the 316 valves after the three and one-half months of service in Period 3.

- Buildup of product solids occurred in the first reactor throughout the test program. Through adjustments made to the reactor system and simulation of the operation in the ADL pilot plant, the cause of the problem was traced to poor agitation and operation during severe upset conditions (e.g., gross overfeeding of lime). While the buildup was never serious enough to cause a shutdown, it did require occasional cleaning. Improved agitation and better process control should reduce such buildup to, at worst, a semi-annual maintenance item. Such maintenance would not require system shutdown in large-scale systems where parallel reactor trains can be used, or the first reactor temporarily bypassed.

Instrumentation

Instrumentation problems primarily involved pH units, level transmitters, and the soda ash feed solution control system.

- The flow-through pH probes originally installed in the system were prone to plugging and/or erosion and failure of probe tips. The flow-through unit in the reactor system was replaced with an immersion unit, which proved to be much more reliable. Modification of take-off lines for flow-through units in the scrubber system and increasing the flow rate minimized problems with these units.

- The level transmitters originally installed were unreliable and required an inordinate amount of instrument maintenance. These were eventually replaced with Foxboro units, which proved to be much more reliable and less prone to failure of critical parts.

- A number of difficulties were encountered with the soda ash feed control system, some of which were related to the wide turndown range for which it was designed. None of the problems affected the operability of the system, since continuous, accurate control of makeup soda ash is not required to replace the small sodium losses in the cake. The principal impact of the difficulties in the feed control system were in the accuracy of the material balances on sodium.

c. Ease of Operation

Ease of system operation was assessed throughout the program either during planned tests of system capabilities under differing conditions or indirectly through inadvertent process upsets and equipment malfunctions. The planned testing included:

- stable operation with low-, medium-, and high-sulfur coal;

- fluctuating load testing (30-100% of design gas rate) with high-sulfur coal; and

- simultaneous particulate removal with high-sulfur coal.

The results of this testing have been discussed.

Indirect measures of the system operability were also obtained during upset conditions. Upset conditions encountered included:

- wide, short-term fluctuations in inlet SO_2;

- wide swings in inlet oxygen concentration;

- inadvertent substitution of limestone for lime in the chemical storage silo;

- gross underfeeding and overfeeding of lime; and
- short-term outages of the filter, first-stage reactor and various instruments with continued operation.

Operation during both the planned variations in system conditions and upsets served to demonstrate the basic stability of the system and the inherent ability of the concentrated lime mode dual alkali technology to withstand sudden (and extended) changes in operating conditions without loss of performance. Of particular note is the fact that close control of pH throughout the system is not required to ensure high SO_2 removal efficiency and prevent scaling. In fact, during some extended periods lasting up to a few days in length the system flows and makeup chemical feed rates were set by inlet and outlet SO_2 and trimmed according to pH's of samples taken from the reactor and scrubber twice per shift.

As oxidation rates changed (due to changes in inlet SO_2 or oxygen concentration of the flue gas), the system chemistry adjusted accordingly. The ratio of sulfate to active sodium in the system liquor simply shifted to effect the appropriate rate of calcium sulfate precipitation required (up to about 25% oxidation).

Similarly, operator errors in setting system flows or makeup chemical feed rates rarely had any immediate effect on system performance, and the effects were usually completely reversed simply by re-establishing proper system conditions.

d. Scale Potential

Due to the low calcium concentrations maintained throughout the system, there was little potential for scale formation. Other than the deposition of solids in the first-stage reactor (previously discussed) the only occurrence of scale formation in the system was the precipitation of calcium carbonate in the absorber during two extended periods when the scrubber system was inadvertently operated well outside the specified pH range. The calcium carbonate was completely dissolved within a few hours by returning the system to normal operating conditions and had no effect on system performance in any way.

The low scale potential, particularly in the scrubber system, is evidenced by the operation of the mist eliminator in the absorber. The mist eliminator was operated without any wash sprays (fresh water or liquor) for the last two operating periods (4,600 hours). No deposit of solids or scale of any form could be found on the mist eliminator following completion of the test program. Similarly, there was no deposit of solids on the reheat gas distributor downstream of the mist eliminator.

II. INTRODUCTION

This is Volume III of a three-volume report for the EPA/ADL Dual Alkali Program. Volume I is an Executive Summary. Volume II covers Task I and Task II, the laboratory and pilot plant tasks of the program of EPA contract No. 68-02-1701 (with IERL, RTP). Volume III covers Task III, the Prototype Test Program performed on the 20-megawatt (nominal) CEA/ADL dual alkali system at Plant Scholz, Gulf Power Company/Southern Company Services, Inc.

The 20-megawatt, prototype dual alkali process was designed and installed by Combustion Equipment Associates, Inc. (CEA) and Arthur D. Little, Inc., (ADL) at the Scholz Steam Plant of Gulf Power Company near Sneads, Florida. This system is one of three advanced technology, prototype flue gas desulfurization systems installed at the plant as part of a technology evaluation program being conducted by Southern Company Services for The Southern Company (an electric utility holding company including Alabama Power Company, Georgia Power Company, Gulf Power Company, Mississippi Power Company, Southern Electric Generating Company, and Southern Company Services, Inc.).

The process was developed and designed jointly by CEA/ADL. Early laboratory research on the process, performed by ADL and sponsored by the Illinois Institute for Environmental Quality, dealt exclusively with characterizing the nature of the regeneration reaction. Based upon the laboratory results, a 2,000 cfm dual alkali pilot plant was constructed at ADL's facilities by CEA/ADL and an eight-month test program sponsored by CEA prior to initiation of the EPA contract was conducted to generate the design data for the prototype system. The pilot system contained the complete dual alkali process loop involving: gas scrubbing; absorbent regeneration; and solids separation. Results of the laboratory program and pilot operations for generation of the prototype system design have been reported previously in the literature.[1]

The laboratory and pilot plant investigation of dual alkali technology has continued at ADL in this program for the U.S. Environmental Protection Agency's (EPA) Industrial Environmental Research Laboratory at Research Triangle Park, N. C. The program involved characterization of the basic process chemistry and the various modes of operation of sodium-based dual alkali processes. The work covered a wide range of flue gas conditions, liquid reactant concentrations, and process configurations including the use of both lime and limestone for regeneration of the sodium scrubbing liquor. This work is reported in Volume II.

Task III, the Prototype Test Program consisted of a one-year test of the 20-megawatt CEA/ADL dual alkali system at Gulf Power. The objective of the program was to characterize the important aspects of the prototype process performance:

- SO_2 removal efficiency;
- oxidation and sulfate formation and control;

- lime utilization;
- waste solids properties;
- sodium makeup requirements and degree of closed-loop operation; and
- process operability and reliability potential.

Construction of the prototype system was completed and the system put in operation in early February 1975. In mid-May 1975, the test program was initiated by ADL, Southern Company Services, CEA, and Gulf Power Company as part of the EPA/ADL Dual Alkali Program.

This report describes the performance of the system over the 17-month period from startup in February 1975 through operations ending in early July 1976.

III. SYSTEM DESCRIPTION

A. PROCESS CHEMISTRY

The CEA/ADL dual alkali SO_2 control process at Scholz Station was an aqueous sodium solution scrubbing system in which the absorbent solution was regenerated using hydrated lime.

The absorption of SO_2 was accomplished using a solution of sodium sulfite, sodium hydroxide and possibly some sodium carbonate (make-up) producing a spent sodium sulfite/bisulfite liquor:

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O \quad (2)$$

$$Na_2CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2 \uparrow \quad (3)$$

$$Na_2SO_3 + SO_2 + H_2O \rightleftarrows 2NaHSO_3 \quad (4)$$

During absorption, and to a lesser extent through the remainder of the system, some sulfite was oxidized to sulfate:

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4 \quad (5)$$

converting an "active" form of sodium to an "inactive" form. Oxidation in the scrubber was generally a function of the scrubber design, oxygen content of the flue gas and the scrubber operating temperature. At excess air levels normally encountered in utility power plant operations (25-40%) burning medium- or high-sulfur coal (> 2% sulfur), the level of oxidation is expected to be on the order of 5-10% of the sulfur dioxide removed.

The scrubber solution was regenerated by reaction with lime which precipitates a mixture of calcium sulfite and calcium sulfate solids for disposal, as shown by the following overall reactions (shown for lime):

$$2NaHSO_3 + Ca(OH)_2 \rightarrow Na_2SO_3 + CaSO_3 \cdot 1/2H_2O \downarrow + 3/2H_2O \quad (6)$$

$$Na_2SO_3 + Ca(OH)_2 + 1/2H_2O \rightarrow 2NaOH + CaSO_3 \cdot 1/2H_2O \downarrow \quad (7)$$

$$Na_2SO_4 + Ca(OH)_2 \rightarrow 2NaOH + CaSO_4 \downarrow \quad (8)$$

After regeneration, the solids were separated from the regenerated liquor and washed. The clear liquor, containing very low amounts of suspended and dissolved calcium, was returned to the scrubbers. Soluble calcium levels are generally less than 100 ppm in concentrated dual alkali processes. Any sodium value lost with the washed waste solids was

replaced by the addition of sodium carbonate to the regenerated liquor, although sodium hydroxide could also have been used since carbonate softening is not required. Since sodium sulfate is also reacted with lime in this system to regenerate sodium hydroxide, it should be possible to use sodium sulfate as the sodium makeup source when low to moderate oxidation levels are encountered.

The system was designed to operate in the concentrated active sodium mode (active Na^+ concentration greater than 0.15M). In this mode, sulfate removal cannot be accomplished by the precipitation of gypsum ($CaSO_4 \cdot 2H_2O$), since the high sulfite levels prevent the soluble calcium concentration from reaching that required to exceed the gypsum solubility product. However, calcium sulfate (in a form other than gypsum) is precipitated along with calcium sulfite ($CaSO_3 \cdot 1/2H_2O$) in the regeneration reactor, resulting in a solid solution of the two salts. The amount of sulfate precipitated in this form is a function of the concentrations of species in solution and the reactor pH. Under normal operation, with sulfate levels up to 1.5M $SO_4^=$, a concentrated mode dual alkali system is capable of keeping up with sulfite oxidation rates equivalent to 25-30% of the SO_2 absorbed without becoming saturated in calcium sulfate.

Additional details of dual alkali chemistry and terminology are given in recent publications[2-7] and in Volume II of this report.

B. SYSTEM CONFIGURATION

The prototype system at the Scholz Steam Plant was installed on Boiler No. 1, a 60-megawatt (nominal) Babcock and Wilcox pulverized coal-fired boiler. The boiler is capable of operating at peak loads of up to 67 megawatts. The prototype was sized to handle 50% of the flue gas from the boiler. The boiler was retrofitted with a sectionalized, electrostatic precipitator capable of 99.5% particulate removal. Sections of the electrostatic precipitator could be de-energized to study the impact of particulate input on process operation.

The design basis for the prototype system is given in Table III-1; a schematic flow diagram is given in Figure III-1. The system, designed as a prototype, incorporated a high degree of flexibility aimed at generating design and operating information for a wide variety of applications. Although the basic mode of operation of the system is a dual alkali process with lime regeneration, the system was designed to accommodate regeneration with limestone alone and regeneration with a combination of limestone and lime. The system was also designed to enable operation as a direct limestone or lime scrubbing system (including simultaneous particulate and SO_2 removal). As a consequence, the system contained equipment and piping in excess of that required to operate a dual alkali system on a boiler already equipped with adequate particulate control.

The venturi scrubber was included in the system to investigate the operation of that type of scrubber in a dual alkali mode (or for direct lime

TABLE III-1

DESIGN BASIS

Flue Gas Inlet	
Flow Rate (acfm)	75,000
(nominal MW equivalent)	20
Temperature (°F)	275
O_2 Concentration (% volume, dry)	6.5 (maximum)
Particulate Loading (gr/scf, dry)	0.02 (precipitator energized)
SO_2 Concentration (ppm, dry)	1,800-3,800
Design Performance	
SO_2 Removal (% reduction)	90 (minimum)
Maximum SO_2 Removal Rate (lb/hr)	1,530
Particulate (gr/scf, dry)	0.02 (no increase in loading)
Power Consumption (% power output)	
with venturi, full spray absorber pump requirements	2.5-3.0
without venturi, with tray absorber pump requirements	1.0-1.5

Prepared by Southern Company Services, Inc.

or limestone scrubbing) when simultaneous particulate and SO_2 removal is required. The second scrubber, an absorption tower, was designed for operation as a tray scrubber, as in a dual alkali system; or as a spray tower, for direct lime or limestone scrubbing. Normally, when simultaneous particulate and SO_2 removal is not required, the system would include only an absorber. In addition to this redundancy in scrubbers, sufficient pump capacity was provided to operate the venturi at an L/G of 25 gallons/Macf of saturated gas and for an absorber L/G of 60 when operating in a spray tower configuration.

An additional storage silo (for limestone), a mix tank and other assorted tanks, pumps, controllers and piping were included in the system to accommodate the high degree of flexibility desired in the prototype system. Except on occasions when limestone was erroneously delivered to the silos instead of lime, the system was operated only in the lime dual alkali mode as shown in Figure III-1.

The system design was based upon removal of at least 90% of the SO_2 in the flue gas for medium- to high-sulfur fuels (up to 5% sulfur). With the precipitator energized, the system was specified not to increase particulate loadings in the scrubber outlet above those in the inlet flue gas.

The power consumption of the system (not including oil for reheat) was equivalent to 2.5-3.0% of the power generated by the unit in producing the flue gas load to the system, with the system operating at full fan capacity (full gas flow at a system pressure drop of 20 inches water) and at full venturi and absorber liquid recirculation capacity. This consumption figure is calculated based upon a nominal 20 megawatts at full load. Correcting for the excess fan and pump capacity, the power consumed by the equipment actually required in this application (tray tower at an L/G of 5-10) is roughly 1.0-1.5% of the power generated at the design conditions. In a full-scale dual alkali system designed for SO_2 removal only (without the venturi), the power consumption should be in this range.

The dual alkali system can be conveniently broken down into three process subsystems: gas scrubbing; absorbent regeneration; and solids dewatering. The design and operation of each of these subsystems is discussed in the following sections.

1. Flue Gas Scrubbing

The gas scrubbing system consisted of a variable-throat, plumb-bob type venturi scrubber followed in series by an absorption tower. A photograph of the scrubbing system is shown in Figure III-2.

Treated flue gas flows through both scrubbers. No provision was included to bypass the gas around either of the scrubber units. Each of these scrubbers was equipped with a removable liquid entrainment separator

Absorption Tower And Deck Venturi Scrubber Forced Draft Fan

FIGURE III-2 GAS SCRUBBING SYSTEM

(although only the entrainment separator in the absorber was installed), an enclosed recycle tank to contain the scrubbing liquor, and two recycle pumps (one operating and one spare). The venturi could be used for absorption and/or particulate control and could be operated on a separate liquor loop from the absorption tower or in series with the absorber liquor loop. The absorption tower can be operated as a tray tower (with up to four trays), as a spray tower, or as a de-entrainment separator.

Gas from the exit of the electrostatic precipitator was forced through the scrubbing circuit using the booster fan provided with the dual alkali system. The fan and motor were designed for a total system pressure drop of 20 inches H_2O at maximum flow. Under normal conditions with the precipitator in service, the venturi was used only for gas saturation (with some attendant SO_2 removal), and a pressure drop of roughly 5 to 10 inches of water was maintained across the venturi.

Gas from the fan entered the venturi scrubber, flowed downward over the wetted approach section and into the high velocity venturi throat. Recycled scrubbing liquor also entered the top of the scrubber through tangential pipe inlets and through a number of vertical bull nozzles equally spaced around the center of the venturi.

After passing through the throat, the flue gas and scrubbing liquor continued downward through the internal downcomer and the liquor was collected at the bottom of the scrubber in the internal recycle tank. At the bottom of the downcomer the flue gas made a 180-degree upward turn and contacted the chevron-type entrainment separator (when used). The entrainment separator was equipped with wash sprays above and below which could be operated continually or on a sequential timing cycle. Either scrubbing liquor or fresh water could be used for washing. During dual alkali operations, this entrainment separator system was not installed.

Following the venturi scrubber, the saturated flue gas entered the bottom of the absorption tower. This tower was designed to operate either as a spray tower, with one or two sets of sprays, or as a tray tower, with from one to four trays. The bottom tray was equipped with a spray underneath to wet the bottom side of the tray. Gas passed upward through the trays and then through a final de-entrainment separator, with a wash system similar to the venturi demister wash. The wash system was used initially, but found to be unnecessary and its use was discontinued.

The clean flue gas leaving the tower was finally reheated by the injection of hot gas from a burner fired with No. 2 fuel oil before being discharged through the stack on top of the absorber. Oil-fired reheat was specified for all the prototype systems in order to reserve steam for power generation.

Regenerated absorbent solution, containing sodium hydroxide, sodium sulfite, sodium sulfate and some sodium carbonate, was mixed with recycle liquor and fed to the top tray of the absorber. The solution flow was countercurrent to the gas through the tray system (two trays) and was collected at the

bottom of the absorber in the internal recycle tank. This collected liquor supplied solution both for spraying the bottom tray and for recirculation to the top tray, as needed for pH control in the scrubber or to maintain liquor flow across the trays.

A bleed from the collected tray tower bottoms was sent forward to the venturi recirculation loop for additional SO_2 removal. In the venturi, the gases with the highest SO_2 concentration were contacted with the most acidic liquor. A continuous bleed stream was drawn from the venturi recirculation loop and sent to the absorbent regeneration system.

2. Absorbent Regeneration

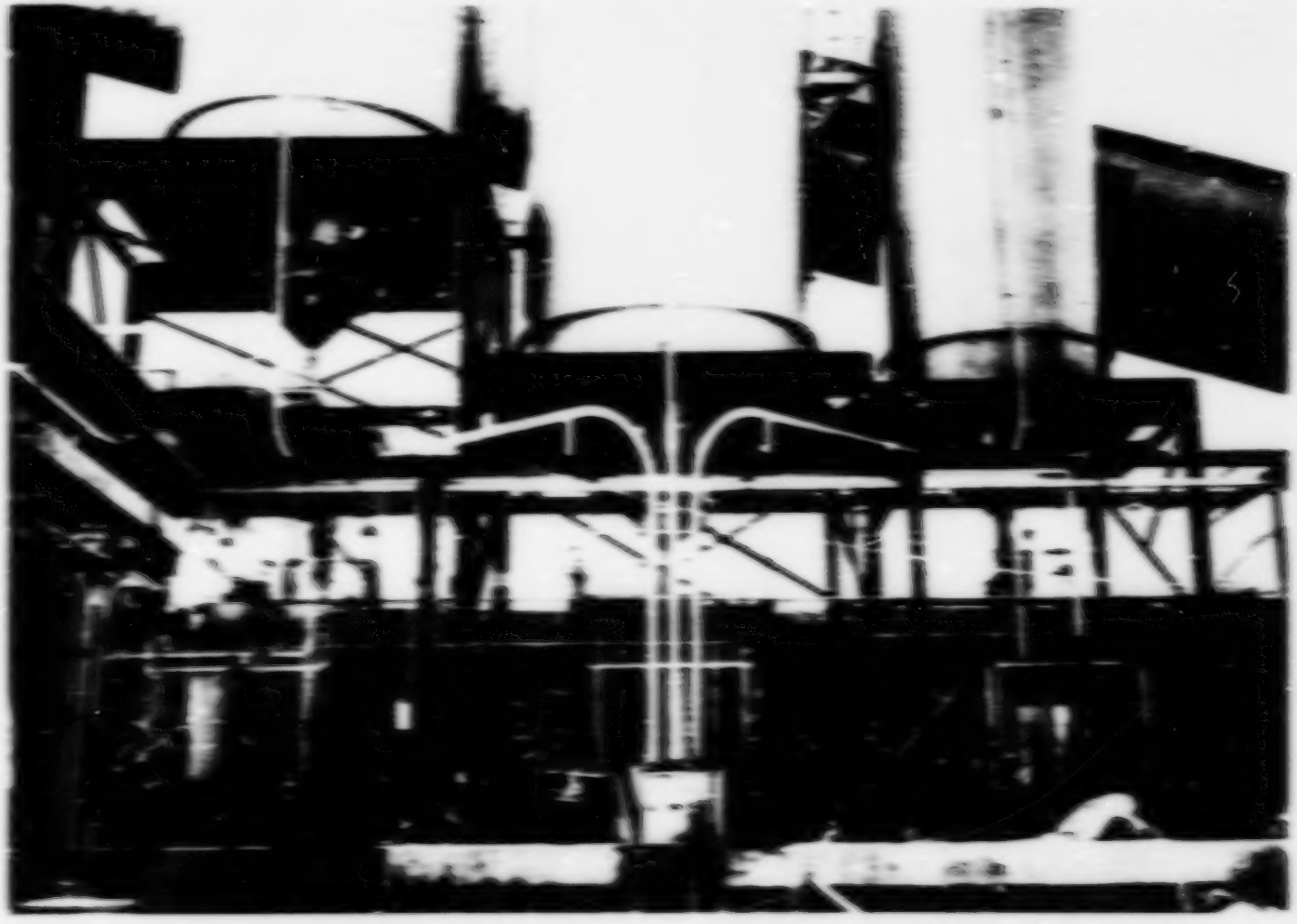
Spent scrubber solution from the venturi recirculation line was bled (on level control) to a two-stage reactor system where it was reacted with hydrated lime. A photograph of the reactor system, chemical storage silos and feed tanks is shown in Figure III-3.

The first-stage reactor, to which both the scrubber bleed and lime were added, had a holdup time of two to ten minutes depending upon the feed forward rate. Slurry from the first stage was fed by gravity overflow to the second-stage reactor, which had a holdup time ranging from 20 minutes to one hour. Both reactor stages were baffled, cylindrical vessels equipped with center-mounted agitators. Initially, the first-stage reactor was a trapezoidal-shaped vessel mounted inside the second-stage reactor. In February 1976 this was replaced with a separate vessel of conventional, cylindrical design.

Hydrated lime was used in this small prototype system for simplicity. It was fed to the first reactor either as a dry solid directly or as a slurry containing from 12% to 12% suspended solids. In a full-scale system, quicklime would normally be slaked and fed as a slurry of 20% to 30% $Ca(OH)_2$. The rate of lime feed was usually adjusted to maintain the pH of the reactor effluent within a preset range (usually 11.5-12.5).

The lime neutralized the bisulfite acidity in the scrubber bleed and further reacted with sodium sulfite and sodium sulfate to produce sodium hydroxide. These reactions precipitated mixed calcium sulfite and sulfate solids resulting in a slurry containing up to 5 wt % insoluble solids.

This two-stage reactor system design has been shown to generate clusters of sulfite/sulfate crystals which are spherically-shaped agglomerates (rosettes) rather than the needle-like or platelet crystals generally associated with calcium sulfite precipitation. These crystal clusters have good settling, filtration, and washing properties and can be generated in the reactor system over a wide range of flue gas and process conditions. The multistage reactor system is part of a process patented by CEA/ADL.



Regeneration Reactor And Dry Lime Storage Silo

Auxiliary Lime Slurry Tank And Storage Silo

Soda Ash Solution Tank And Storage Silo

FIGURE III-1 ABSORBENT REGENERATION AND CHEMICAL MAKEUP SYSTEM

3. Solid/Liquid Separation and Solids Dewatering

Slurry from the regeneration reactor system was fed to the center well of the slurry thickener. The 40-foot diameter thickener was sized to handle the solids produced from the treatment of flue gases from the full 40 megawatts of Boiler No. 1 (in contrast to the scrubber and reactor systems which were sized to handle 20 megawatts). Figure III-4 shows a photograph of the thickener at Scholz.

The thickened slurry from the bottom of the settler was sent to a rotary drum vacuum filter, also shown in Figure III-4. The solids content of the underflow was maintained below 30% for ease of underflow pumping. The slurry was recirculated past the filter in a recycle loop that returned the slurry to the solids zone in the settler. The feed to the filter was drawn as a bleed from this recirculation loop. The filter surface area was 75 ft^2.

The cake was washed on the filter using from two to four water spray bars arranged in series. This wash removed a large fraction (up to 95%) of the occluded soluble salts from the cake and returned these salts to the system, thereby reducing sodium losses and minimizing sodium carbonate makeup.

Solids from the filter were retained in a solids storage enclosure directly under the filter from which they were loaded into dump trucks for transfer to the disposal area. The mixed filtrate and wash liquor from the filter were returned to the thickener.

The disposal area for the dual alkali waste cake was a one-acre pit (450 ft x 100 ft) approximately 12 feet deep. The bottom and sides of the pit were lined with a layer of clay covered by a double thickness of polyethylene liner. The polyethylene was reinforced between the sheets with a mesh of nylon fiber. The floor of the pit was sloped to a single collection drain constructed of PVC from which leachate was discharged to the ash pond. On top of the polyethylene liner was a two-inch layer of sand and gravel.

Makeup sodium carbonate was fed to the thickener in order to allow for easy removal of any $CaCO_3$ precipitated. This carbonate was not intended for use as a softener, since soluble calcium concentrations in the regenerated liquor generally run less than 100 ppm. However, some $CaCO_3$ precipitation occurs due to its very low solubility limits. The amount of $CaCO_3$ formed will generally be very small, a few hundred pounds per day at design conditions, or less than 0.5% of the total cake produced. Provisions were made to prepare soda ash solution using either river water or solution liquor.

Clear liquor overflow from the thickener is collected in the thickener hold tank which acts as surge capacity for the absorbent liquor feed to the scrubber system. Water was normally added to this hold tank to make up for the difference between total system water losses (evaporation and cake moisture) and total water inputs from other sources (sodium makeup solution, pump seals, lime feed, cake wash, and demister wash).

Figure 11-111. Damaged Fuel Tank

IV. OPERATING HISTORY

A. GENERAL OPERATING CONDITIONS

The prototype system commenced process startup on February 3, 1975 and was operated over a period of 17 months through July 3, 1976, when the system was shut down at the completion of the test program. During these 17 months the system logged 7,128 hours of operating time with shutdown periods of varying length for system maintenance and modifications and when the boiler was taken off line. The 17 months of operation can be logically broken down into three discrete operating periods as defined by the flue gas composition and coal characteristics, and by the mode of system operation. These three periods of operation are summarized in Table IV-1.

During the first two operating periods, covering the first 11 months of operation, the system treated flue gas with lower sulfur dioxide concentrations and higher oxygen levels than the range for which the system was originally designed. This represented a difficult test for the prototype system. In sodium-base dual alkali systems for a given scrubber design and soluble solids levels, the rate of sulfite oxidation (mols per unit time) is a strong function of the oxygen concentration in the flue gas and is relatively independent of the rate of sulfur dioxide removal (mols per unit time). As oxygen concentrations increase and SO_2 concentrations decrease, a higher percentage of the SO_2 removed from the flue gas is converted to sodium sulfate rather than sodium sulfite/bisulfite in the scrubber liquor. This higher percentage oxidation requires an increase in precipitation of sulfate relative to sulfite and a higher calcium sulfate content in the precipitated calcium sulfite/sulfate to enable closed-loop operation with no intentional purging of sodium sulfate.

Sulfur dioxide concentrations in the flue gas averaged between 1,100 and 1,200 ppm, compared with a minimum design concentration of 1,800 ppm during the first two operating periods. The actual concentrations varied over a range of from 600 to 1,600 ppm, often fluctuating daily and even hourly over the entire range of concentrations. Oxygen concentrations in the flue gas entering the scrubber ranged from 9% to 11% by volume (equivalent to 30-100% excess air) with oxygen levels increasing with decreasing boiler load (higher excess air). During the first operating period, air leaks in the boiler combustion air preheater and coal feed tubes contributed from 0.5 to 2.0 volume % to the oxygen concentrations. Oxygen levels in the flue gas were reduced from the 7-10% range down to the 3-7% range in September 1975 after air preheater repairs and when burner box pressure was brought under better control.

During the third period of operation the system was tested on high sulfur coal. In addition to stable load testing, as conducted during Periods 1 and 2, testing also included fluctuating load testing and particulate testing during which time the electrostatic precipitators were partially or completely de-energized.

TABLE IV-1

SUMMARY OF OPERATING PERIODS

	Operating Periods		
	1	2	3
Inclusive Dates	2/3/75-7/18/75	9/16/75-1/2/76	3/16/76-7/3/76
Operating Hours	2,537	2,180	2,411
Coal	Low Sulfur	Low/Medium Sulfur	High Sulfur
Testing	Startup & Shakedown	Stable Load	Stable Load Fluctuating Load Particulate

The general process operating conditions during each of the three operating periods are discussed in the next section.

6. DESCRIPTION OF OPERATING PERIODS

1. Operating Period 1 -- Startup and Initial Operations

This first operating period extended from initial startup on February 1, 1975 through July 18, 1975, when the system was shut down for a two-month period for modifications and repairs, and to await receipt of replacement parts. During this operating period, the system was operated approximately 2,540 hours, 79.0% of the time that the boiler was in operation. More than half of the entire system downtime of 670 hours relative to the boiler is accounted for by a three-week shutdown in mid-April, after the start-up period, when necessary maintenance was performed and equipment modifications and adjustments were made prior to the start of the formal EPA test program in mid-May. These modifications were to enhance the system operability and performance under the low-sulfur coal conditions -- conditions for which the system was not originally designed. Equipment changes are described in Chapter V.

Table IV-2 contains a summary of the fuel and flue gas characteristics encountered during this operating period. The boiler was fired with a combination of several medium- and low-sulfur coals ranging in sulfur content from 0.9 to 2.2 wt %. A plot of coal analyses for daily coal samples is presented in Appendix A. The weighted average sulfur content of the coal as burned was 1.6 wt %, producing an average SO_2 level in the flue gas of about 1,050 ppm. Since it was not possible to segregate and fire the different coals selectively, the SO_2 levels in the flue gas fluctuated daily and often hourly from a low of 600 ppm to a high of 1,550 ppm.

The flue gas load to the prototype system was kept within a range equivalent to 15-23 megawatts (39,000-60,000 inlet scfm, wet basis), and typically ran about 17 megawatts (44,000 inlet scfm). However, during Period 1 the boiler load varied from 15 megawatts to 47 megawatts with attendant variation in excess air rates.

In addition to the unfavorable process conditions resulting from low-sulfur coal and the high oxygen concentrations, there were frequent process upsets. These upsets included occasional carryover of fly ash with the flue gas and the inadvertent contamination of the lime supply with limestone (caused by a mix-up in the lime and limestone deliveries to the prototype systems at the plant). While the presence of fly ash in the system caused little or no effect on operation or performance, the limestone did produce temporary changes in the process chemistry -- particularly when a significant fraction of the calcium feed to the reactor was limestone.

The limestone usually appeared mixed with lime at levels of up to 50% of the total feed; however, on a number of occasions (for periods lasting

TABLE IV-2

SUMMARY OF SYSTEM INLET CONDITIONS

Operating Period 1 (2/75 - 7/75)

	Range	Average
Coal Fired:[a]		
Sulfur (wt %)	0.9-2.3	1.6
HHV (Btu/lb coal)	11,500-13,000	12,000
Chloride (wt %)	0.03-0.10	0.08
Ash (wt %)	6.2-19.2	12.9
Inlet Gas:		
Gas Load Treated (MW equiv.)[b]	15-22	17
SO_2 Level (ppm-dry basis)	600-1,550	1,050
O_2 Level (% dry vol.)	5.0-11.0	7.5
Particulate Loading (grs/scfd)	<0.02	--

[a]Based on analyses of daily coal samples (as fired).

[b]Based upon a nominal 20 MW design load.

up to one day) the feed to the reactor system was pure limestone. During periods when only limestone was fed to the reactor, the pH in the reactor system dropped, SO_2 removal decreased somewhat and waste cake properties deteriorated slightly. Normal process conditions were re-established after the limestone passed through the system.

There was a general rise in the flue gas oxygen concentration over the operating period due to worsening leakage in the boiler air preheater section. By mid-July oxygen concentrations were in the 8-10% range, with dilution of the already low SO_2 levels down to about 850-950 ppm. At the resultant high oxidation rates (30-50% of SO_2 removal), active sodium levels were inadvertently allowed to drop below 0.15M, into the range of dilute mode dual alkali operation. Under these conditions, soluble calcium levels in the regeneration system rose and the regenerated liquor became saturated in calcium sulfate, resulting in some gypsum scaling of the piping at the outlet of the regeneration reactor. At the same time, mechanical problems in the scrubber system (failure of two control valves and a pinhole leak in the absorber recycle tank) required that the system be shut down for repairs.

Based upon this experience, it was decided that in future operations the active sodium concentration would be maintained well above the 0.15M level by operating with a slightly higher total sodium concentration in the system. This would allow the sodium sulfate concentration to increase in the system during periods of increasing rates of oxidation. Sulfate levels would continue to rise relative to the sulfite until the rate of sulfate precipitation as a calcium salt equaled the rate of oxidation. This can be accomplished without reverting to dilute mode operation at oxidation rates up to about 25-30% of the SO_2 removal rate.

The system was shut down from mid-July until mid-September. Repairs and revisions made during this period were of a mechanical nature rather than involving process changes and are discussed later. After shutdown it was decided to await the repair of the preheater leak rather than attempt to continue operating at the low SO_2 concentrations and increasing oxygen concentrations. About two-thirds of the shutdown period was to await replacement parts for the valves that had failed.

2. Operating Period 2 -- Low- to Medium-Sulfur Coal Operation

The system was put back in operation on September 16, 1975. From mid-September to mid-October repairs were made to the air preheater during boiler outages and adjustments were made in the boiler operation, reducing flue gas oxygen levels down to the 5-6% range. For the remainder of the test period through January 2, 1976, oxygen concentrations were generally kept in the 5-6% range. As shown in Table IV-1, SO_2 levels were slightly higher than those encountered during the first operating period, with an average level of about 1,200 ppm (a plot of coal analyses for daily coal samples is presented in Appendix A). The gas load to the system was in the same range as that for Period 1.

TABLE IV-1

SUMMARY OF SYSTEM INLET CONDITIONS

Operating Period 2 (9/75-1/76)

	Range	Average
Coal Fired:[a]		
Sulfur (wt %)	1.5-3.1	2.0
HHV (Btu/lb coal)	11,900-14,100	13,000
Chloride (wt %)	0.02-0.14	0.08
Ash (wt %)	8.8-21.0	13.9
Inlet Gas:		
Gas Load Treated (Mw equiv.)[b]	16-19	18
SO_2 Level (ppm-dry basis)	800-1,700	1,250
O_2 Level (% dry vol.)	4.5-9.5	6.0
Particulate Loading (grs/scfd)	<0.02	--

[a] Based on analyses of daily coal samples (as fired).

[b] Based upon a nominal 20 Mw design load.

Active sodium concentrations were maintained in a range for concentrated mode operation by the slightly higher SO_2 levels and lower oxygen concentrations and by operating with a slightly higher total sodium concentration. Continuing improvements were also made in the mechanical performance of system components, particularly the filter. One unprogrammed period of regeneration with limestone occurred in this interval.

During this period, until shutdown on January 2, 1976, the prototype system logged approximately 2,180 hours of operation, which corresponds to 97.1% of the time the boiler was in operation.

3. Operating Period 3 -- High-Sulfur Coal Operation

During the boiler maintenance outage in January and February 1976 a number of system modifications were made. These included equipment adjustments to improve operability and provide for additional flexibility in testing during Period 3, as well as inspection and maintenance of all equipment. Among the improvements were the installation of a new first-stage reactor vessel to replace the original one (to improve mixing) and modification of the lime slurry feed system for use during the third test period. The original first-stage reactor had been mounted inside the second-stage reactor and had a trapezoidal cross-section; the new reactor was of standard cylindrical design and was mounted external to the second reactor.

Operating conditions during the third operating period are summarized in Table IV-4. The coal fired was a high-sulfur, Alabama coal ranging in sulfur content from 4.4% to 5.1% and averaging 3.5% (based upon analyses of daily grab samples). Inlet SO_2 levels experienced ranged from as low as 1,900 ppm (on rare occasions) to almost 3,000 ppm. Typical inlet SO_2 levels were 2,250 $\pm$ 300 ppm.

Oxygen levels in the flue gas during Period 3 were similar to those experienced in Period 2 after repairs on the air preheater were completed. Oxygen concentrations varied from 4.9% to as high as 9.0%, but typically ranged from 5.5% to 7.5%.

Testing during Period 3 included 10 weeks of operation under relatively stable conditions, three weeks of operation at fluctuating gas load (30-100% of design load) and two weeks of particulate testing (with the precipitator either partially or completely de-energized). Over this period the system operated a total of 2,411 hours, or 93.2% of the time that the boiler was in service. The total downtime during this period is due to a number of short-term outages (e.g., to repair a broken coupling on the agitator in the second-stage reactor).

TABLE IV-4

SUMMARY OF SYSTEM INLET CONDITIONS

Operating Period 3 (3/76-7/76)

	Range	Average
Coal Fired:[a]		
Sulfur (wt %)	2.4-5.1	3.5
HHV (Btu/lb coal)	10,000-13,200	12,200
Chloride (wt %)	0.01-0.20	0.11
Ash (wt %)	9.3-22.3	12.3
Inlet Gas:		
Gas Load Treated (MW equiv.)	6-20	--[b]
SO_2 Level (ppm-dry basis)	1,500-2,800	2,250
O_2 Level (% dry vol.)	4.5-9.0	--[c]
Particulate Loading (grs/scfd)	0.01-3.2	--[c]

[a] Based on analyses of daily coal samples (as fired).

[b] Gas load averaged about 18 MW equivalent during stable load testing and 13 MW during fluctuating load testing (based upon a nominal 20 MW design load).

[c] Particulate loadings were <0.02 grs/scfd except during particulate testing.

V. SYSTEM PERFORMANCE

The purpose of installing the prototype system was to test the process chemistry and design on this relatively small scale in order to evaluate the viability of the process technology for large-scale utility applications. The prototype system represented a scale-up factor of about 40 over the CEA/ADL dual alkali pilot plant. The modular units for a large-scale utility system would correspond to a further scale-up factor of 5 to 10 over the prototype system design capacity. While the overall reliability and operability of the process were a principal concern, the system was not intended to be a demonstration unit nor a test of the ultimate availability of such systems when applied full scale. The test program at Scholz, therefore, was focused on characterizing the process chemistry under different operating conditions, verifying process and equipment design parameters, and defining the process capabilities. Overall the system performance was excellent. During the more than 7,100 hours of operation, the prototype system demonstrated the capability of the concentrated mode dual alkali system to handle flue gas from a wide range of coals (from as low as about 1.5 wt % sulfur) with no loss in SO_2 removal efficiency or significant deterioration in operability or waste cake properties. There were, of course, equipment problems as would be expected with a test system. Some of these caused short-term outages and loss of availability; however, none were symptomatic of any deficiencies in the process technology.

The following discussion of the system performance covers the entire 17-month period of operation from startup in February 1975 through completion of the test program in July 1976. The discussion is broken down into three parts: (1) availability; (2) process performance; and (3) mechanical (equipment) performance. Emphasis has been placed on process performance, since it ultimately defines the capabilities and viability of the concentrated mode dual alkali technology. System availability and mechanical (equipment) performance are of principal interest with regard to how these reflect and affect the overall projected reliability, operability and cost of the technology when applied full-scale.

A. AVAILABILITY

In reviewing the system availability, it is worth noting that the only spares in the prototype system were pumps. There was no redundancy or spare capacity in any of the major process units. There was one scrubber train, one reactor system, one lime feed system (slurry or dry), one thickener, and one filter. Multiple trains and/or spare capacity for the units would normally be incorporated in full-scale applications. Such redundancy would allow downtime at convenient, scheduled times for even the most trivial maintenance requirements without causing loss of availability or even necessarily curtailment of power generation.

Despite the lack of redundancy in major pieces of equipment and the difficult flue gas conditions encountered during the first operating period, the availability record of the prototype system over the entire 17 months of operation is impressive.

Boiler and prototype system operating hours are graphically displayed by month in Figure V-1 and summarized by operating period in Table V-1. Appendix B contains a list of boiler and system outages, the duration of each outage, and the reason for the shutdown.

The availability during the first operating period, 79.0%, includes the initial startup of the system and the three-week shutdown period for system adjustments and modifications prior to the start of the EPA test program. These adjustments included normal process refinements expected during system shakedown as well as modifications required to handle the low-sulfur coal conditions -- conditions for which the system was not designed. During the second operating period, system availability was 97.1%; and during the third operating period, system availability was 93.2%. These availability figures correspond closely to the PEDCo definition of system operability since they reflect only hours the system was actually in operation.

During the two months between the first and second operating periods, the system was down for maintenance. This outage was prolonged by delays in shipment of spare parts and completion of repairs to the boiler air preheater to correct excessive air leakage. In January and February 1976 the boiler was down for six weeks for scheduled maintenance. The system was down for an additional four weeks to complete modifications and repairs begun in January.

The last two weeks of system downtime resulted from a delay in the return of the filter drum which was being modified. Including these extended shutdown periods in the availability calculation, overall system availability for the entire program was 70.2%. Exclusion of these two interim periods from the calculation yields availability during operating periods of 88.6%.

B PROCESS PERFORMANCE -- STABLE LOAD OPERATION

1. Overall Operation

The general process conditions for the three operating periods are summarized in Tables V-2, V-3, and V-4. Control plots (plots of operating conditions versus time) for the entire 17 months of operation are given in Appendix C. Appendix D shows process flows and stream compositions for typical days during each operating period. Appendix E gives correlations of solution composition with pH based upon analyses of the scrubber bleed and reactor effluent liquors.

The system operating philosophy during Period I was to maintain the active sodium concentration in the system at or above 0.2M Na^{+} and to maintain a

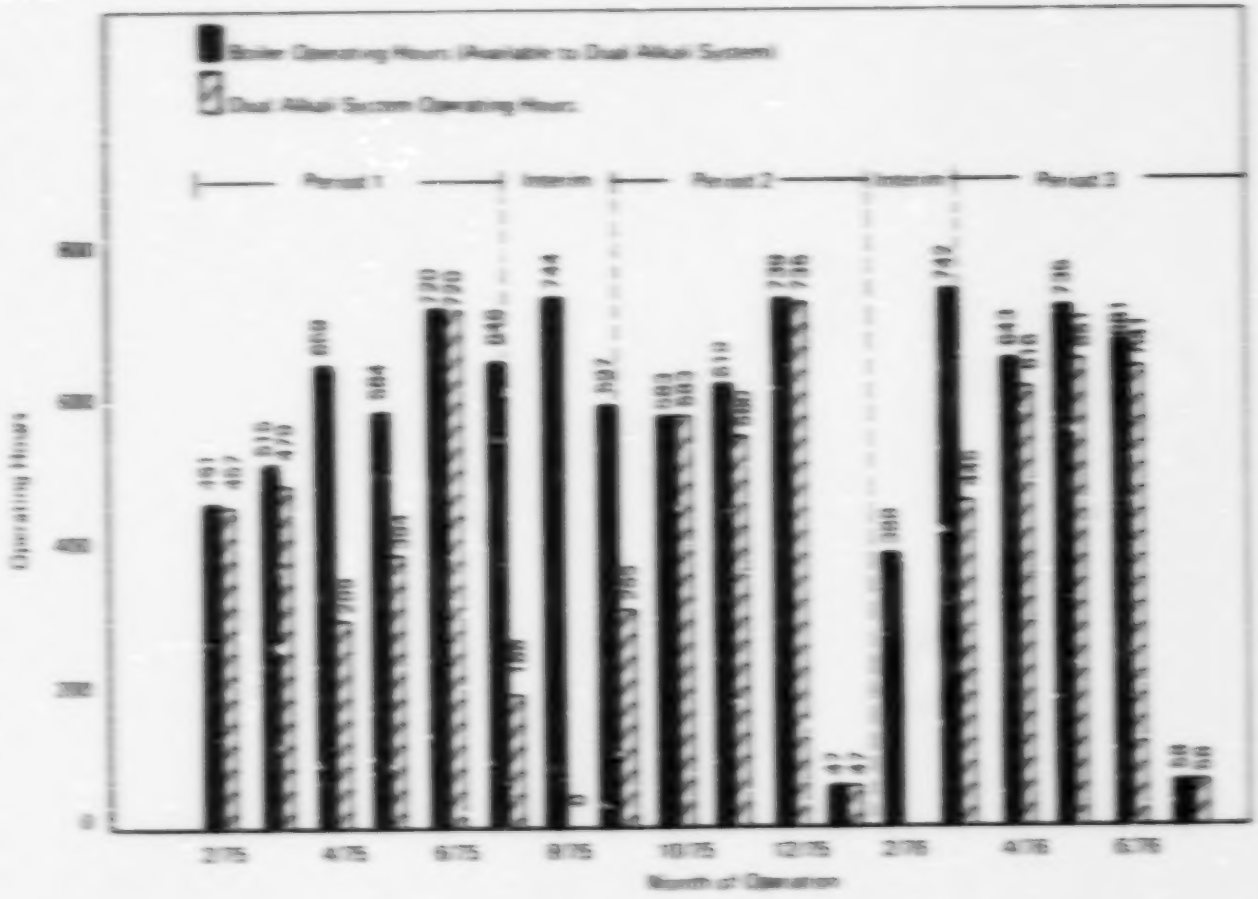


FIGURE V–1 AVAILABILITY OF THE CEA/ADL DUAL ALKALI SYSTEM AT SCHOLZ

TABLE V-1

SUMMARY OF PROTOTYPE SYSTEM AVAILABILITY

	Dates	Operating Hours		Availability
		Prototype	Boiler[a]	Prototype Hours as percent of Boiler Hours
Operating Period 1	2/3/75-7/18/75	2,537	3,211	79.0
Interim Period	7/18/75-9/15/75	0	1,460	0
Operating Period 2	9/16/75-1/3/76	2,160	2,244	97.1
Interim Period	1/3/76-3/15/76	0	698	0
Operating Period	3/16/76-7/3/76	2,411	2,588	93.2
Total Operating Periods		7,128	8,043	88.6
Total Program		7,128	10,161	70.2

[a]Hours boiler available to dual alkali system

TABLE V-2

SUMMARY OF SYSTEM OPERATING CONDITIONS - PERIOD 1
(3/75 - 6/75)

	Range	Average
Inlet Gas:		
Gas Load Treated (MW equiv.)[a]	15-22	17
SO_2 Level (ppm - dry basis)	600-1,550	1,050
O_2 Level (% dry vol.)	5.0-11.0	7.5
	Range[b]	**Typical[b]**
Regenerated Liquor Composition:		
pH	10-12.6	11-12.5
Na^+_{act} (M)	0.10-0.35	0.2-0.25
$SO_4^=$ (M)	0.60-1.05	0.7-0.9
Cl^- (ppm)	3,000-7,000	4,000-5,500
Ca^{++} (ppm)	20-800+[c]	50-200

[a] Based upon 20 MW (nominal) design basis.

[b] Not including periods when limestone fed to reactor.

[c] Ca^{++} levels above 350 ppm occurred during the period just prior to and during the dilute mode operation.

TABLE V-1

SUMMARY OF SYSTEM OPERATING CONDITIONS - PERIOD 2
(10/75 - 12/75)

	Range	Average
Inlet Gas:		
Gas Load Treated (Mw equiv.)[a]	15-19	18
SO_2 Level (ppm - dry basis)	800-1,700	1,200
O_2 Level (% dry vol.)	4.5-9.5	6.0
	Range[b]	Typical[b]
Regenerated Liquor Composition:		
pH	10-12.8	11-12
Na^{+}_{act} (M)	0.25-0.6	0.3-0.35
$SO_4^{=}$ (M)	0.6-1.05	0.8-1.0
Cl^{-} (ppm)	1,000-2,100	1,300
Cu^{++} (ppm)	90-160	70

[a]Based upon 20Mw (nominal) design load.
[b]Not including periods when limestone fed to reactor.

TABLE V-A

SUMMARY OF SYSTEM OPERATING CONDITIONS - PERIOD 3, STABLE LOAD TESTING
(4/76 - 9/76)

	Range	Average
Inlet Gas:		
Gas Load Treated (Mw equiv.)[a]	16-19	18
SO_2 Level (ppm-dry basis)	1,500-2,800	2,300
O_2 Level (% dry vol.)	4.5-9.0	6.5
Regenerated Liquor Composition:	Range	Typical
pH	10-12.8	11.5-12.3
Na^{+}_{act} (M)	0.35-0.45	0.35-0.4
$SO_3^{=}$ (M)	0.65-0.75	0.7-0.75
Cl^{-} (ppm)	7,500-11,500	9,000-11,000
Ca^{++} (ppm)	(80-100)[b]	(60)[b]

[a] Based upon 80 Mw (nominal) design load.

[b] Estimated -- only a few data points taken.

total sodium concentration sufficient to allow soluble sulfate concentrations high enough to precipitate calcium sulfate roughly at the rate of sulfate formation. This resulted in a fairly stable operation at about 2.0M total sodium (~ 0.8M $SO_4^{=}$) until the end of June, when the inlet SO_2 level fell to 850-950 ppm and oxygen levels rose to 8.5-10.0%. Under these conditions, without an increase in the total sodium concentration by increasing the sodium carbonate feed rate, the system chemistry drifted into the range of a dilute dual alkali mode with active sodium concentrations dropping to below 0.15M Na^+. Except for the two-week period of dilute mode operation in July, the thickener liquor typically contained 0.20-0.25M active sodium, 0.7-0.9M sodium sulfate, and 0.10-0.15M sodium chloride (4,000-5,500 ppm Cl^-).

At the start of Period 2, it was decided to maintain the active sodium concentration in the system above 0.3M Na^+ and to allow the sodium sulfate concentration to fluctuate to any level necessary to maintain an equilibrium between sulfite oxidation in the system and sulfate precipitation. This would prevent any possibility of deterioration of the system chemistry to that of a dilute mode.

With the slightly improved flue gas conditions (higher inlet SO_2 and lower oxygen levels) stable conditions were achieved at sodium sulfate concentrations in the range of 0.8-1.0M. Chloride concentrations leveled out at 0.03-0.06M (1,300 ppm Cl^- average). Routine analyses of coal samples performed for the plant from both Periods 1 and 2 show about the same chloride content, approximately 0.08 wt % on the average. However, the accuracy of the analytical technique was only about ± 0.05 wt %.

During the third operating period with high-sulfur coal the system was operated under relatively stable flue gas conditions (gas load and composition) from mid-March to the last week of May 1976, when fluctuating load testing was begun. At the high inlet SO_2 levels experienced during Period 1, active sodium concentrations stayed above 0.35M Na^+ with about the same total sodium concentrations as in the prior two operating periods. This reflected the lower oxidation rate (as a percentage of SO_2 absorbed) and the lower sulfate concentration required to keep up with oxidation (as will be discussed later). Chloride concentrations, though, rose to over 10,000 ppm due to the increased chloride content of the high-sulfur coal.

Table V-5 shows the overall system performance in terms of SO_2 removal, makeup chemical requirements, and waste solids properties for material balance intervals in each operating period. The performance data for Periods 2 and 3 are based upon overall material balances derived from flue gas analyses, waste cake properties and production rates, and makeup chemical inventories. Complete material balances were not attempted for Period 1 because installation of the truck scale for weighing cake was not completed until the end of June 1975. The accuracy of material balances was limited by the fluctuating gas load and SO_2 levels, contamination of the lime supply with limestone (Periods 1 and 2), and occasional instrumentation problems. The accuracy

TABLE VI-5

SUMMARY OF OVERALL SYSTEM PERFORMANCE
BENCH-SCALE LOAD TESTING

(April 1975 – June 1976)

Balance Period		Coal Sulfur Content	SO_2 Removal Efficiency (% of Inlet)	Lime Feed Stoichiometry (moles $Ca(OH)_2$/mol ASO_2)	Soda Ash Feed Stoichiometry (Equiv moles Na_2CO_3/mol ASO_2)	Waste Cake Solids Content (wt %)
No.	Dates					
1	4-6/75	Low	95[a]	~ 0.95	—[c]	48
2	11-12/75	Low/Medium	96[b]	0.95	0.965	51
3	4-5/76	High	97[b]	0.985	0.980	54

[a] Data represents weighted average of periods with venturi only and venturi and demister

[b] Venturi and demister

[c] Insufficient data

of short-term material balances was also affected by the inability to measure silo inventories accurately, particularly for sodium carbonate, for which there was a large inventory and a low feed rate.

The various aspects of the process performance during each period are discussed in the following sections, according to the following six performance characteristics:

- SO_2 removal;
- lime utilization;
- oxidation and sulfate control;
- waste cake properties;
- sodium makeup; and
- process operability and reliability potential.

A. SO_2 Removal

The scrubber system was operated using two different configurations for SO_2 removal: the venturi and absorber together in series (with two trays) and the venturi alone. In the latter configuration the trays were not removed from the absorber; rather, the regenerated liquor feed to the top tray was diverted either to the absorber recycle tank (from which it was transferred to the venturi) or bypassed directly to the venturi through a line installed in May 1975. (The bypass line was not in the original design, since the operation on low-sulfur coal was not anticipated.) When the absorber was not used, the recycle flow to the top tray and the flow to the spray on the underside of the bottom tray were both discontinued; however, the absorber pumps were maintained in operation to transfer liquor collected in the absorber tank to the venturi. In order not to exert excessive back-pressure on the absorber pumps, a recycle was maintained through an open spray header during intervals when there was no feed to the trays. This open recycle did offer a minimal amount of gas/liquid contacting in addition to the venturi, since the recycle resulted in a falling film of liquor.

During Period 1, both operational configurations were used at different times. However, during Periods 2 and 3, only the combined venturi and absorber configuration was used.

The SO_2 removal efficiency achieved with each of these configurations is shown in Figure V-2 for intervals when the inlet SO_2 concentration ranged from 1,050 to 1,250 ppm (Periods 1 and 2). Figure V-3 shows the SO_2 removal achieved as a function of pH at the higher inlet SO_2 levels (1,900-2,300 ppm) in Period 3. Points shown on these plots represent data taken during the normal course of operations when inlet and outlet SO_2 levels and system pH's were simultaneously available and

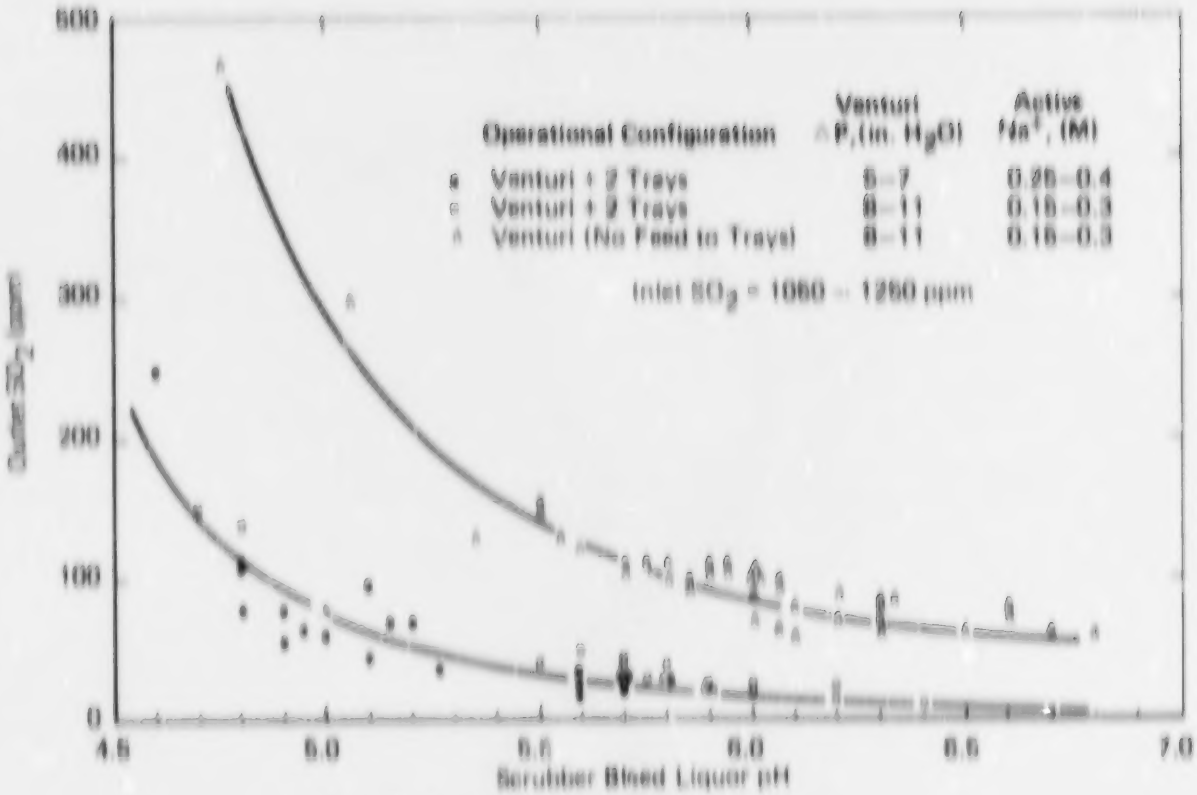


Figure V–2 SO_2 Removal as a Function of pH – Low/Medium-Sulfur Coal

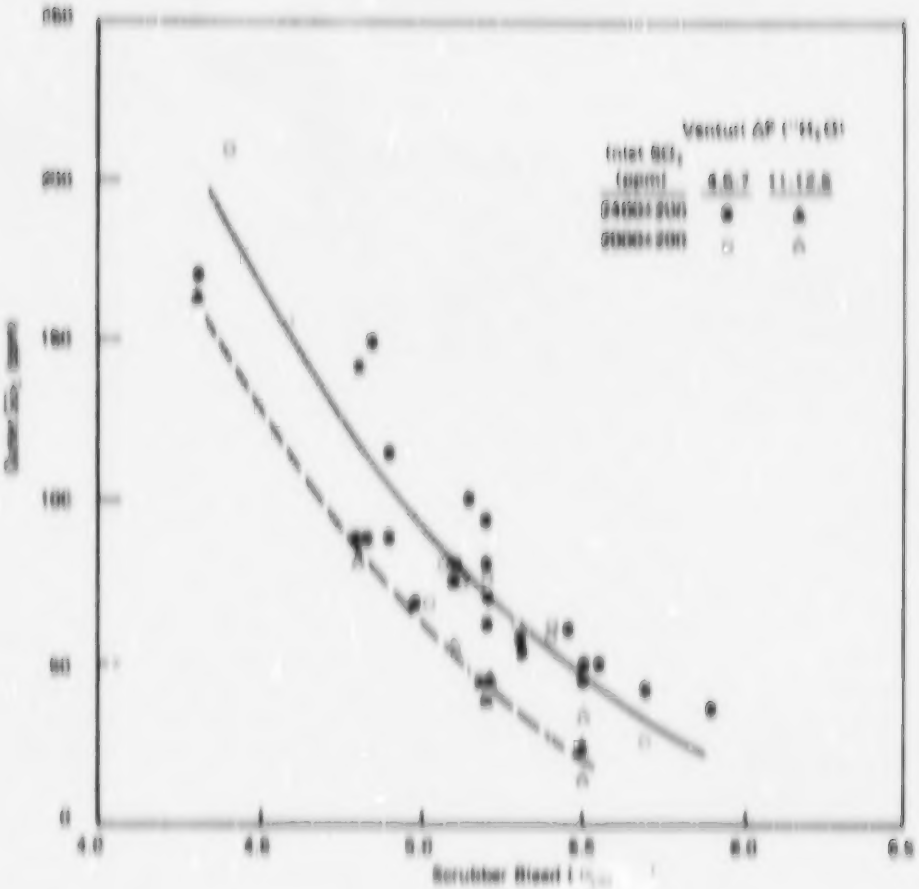


FIGURE V-3 SO_2 REMOVAL AS A FUNCTION OF pH— HIGH-SULFUR COAL

confirmed. In most cases, each data point represents at least a few hours of operation at the condition shown. Where such a continuum of data exists, outlet SO_2 levels and pH's have been averaged and rounded to the nearest 5 ppm and 0.05 pH units, respectively. Table V-6 summarizes the overall SO_2 scrubbing performance at Scholz from April 1975 through June 1976, when the outlet SO_2 monitor was operational.

The data in Figures V-2 and V-3 and Table V-6, which reflect the general operating experience at Scholz, confirm the high SO_2 removal capability of sodium solution scrubbing systems operating in a similar concentration range of active sodium (0.2-0.4M Na^+). Achieving a given outlet SO_2 level (within the limit of the number of contact stages in use) was essentially a matter of adjusting the operating pH of the scrubber system by changing the feed forward rate and/or pH of the regenerated liquor. Over the 15 months of operation between April 1975 and July 1976, the average SO_2 removal using both the venturi and absorber was 95.5% (with low- and high-sulfur coal); and with the venturi alone, was 90.7% (low-sulfur coal only).

As indicated in Figures V-2 and V-3, outlet SO_2 levels and SO_2 removal efficiency were primarily a function of the inlet SO_2 level, scrubber configuration (venturi versus venturi plus trays), pH and, to a lesser extent, venturi pressure drop. At inlet SO_2 levels of 1,050-1,250 ppm, and using both the venturi (ΔP = 5-11 inches of water) and absorber (two trays), outlet SO_2 levels below 50 ppm could be easily achieved at venturi bleed liquor pH's above 5.2. At these low inlet SO_2 levels, a 50 ppm outlet level corresponds to better than 95% removal efficiency. Operation at higher pH's resulted in higher SO_2 removal efficiency; however, there was little to be gained by operating at pH's much in excess of 6.0. Above a pH of 6.0, outlet SO_2 levels dropped to 20 ppm or less (> 98% removal), taxing the accuracy and operating range of the outlet SO_2 monitor.

At higher inlet SO_2 levels (1,900-2,800 ppm) the experience was much the same, although achieving the same outlet SO_2 level (which would correspond to a higher removal efficiency) required a slightly higher pH. To achieve 50 ppm outlet SO_2 (~ 98% removal), a pH of about 5.5 was required at about 2,400 ppm inlet SO_2 compared with a pH of 5.2 at 1,200 ppm.

For the most part, when both the venturi and absorber were operated together, the pH of the venturi bleed liquor was maintained between 4.8 and 5.9 to ensure better than 90% SO_2 removal. With the low inlet SO_2 levels of Periods 1 and 2 (600-1,700 ppm) this resulted in outlet SO_2 generally ranging from 15 to 100 ppm. At the higher inlet SO_2 levels of Period 3 (April and May 1976), the outlet SO_2 typically ranged from 25 to 150 ppm.

The effect of venturi pressure drop on SO_2 removal with both trays in operation is also shown in Figures V-2 and V-3. At low inlet SO_2 levels there was no discernible effect of venturi pressure on SO_2 removal over

[redacted]

[redacted]

[redacted]

the range of pressure drop from 5 to 11 inches of water. At high inlet SO_2 levels in Period 2 there was a small but significant increase in SO_2 removal efficiency by increasing the venturi pressure drop from 6 to 7 inches of water to about 12 inches of water. The increase in pressure drop reduced outlet loadings by 10 ppm to 30 ppm over a pH range of 6.3 to 5.5.

Use of the venturi alone for SO_2 removal (no feed of regenerated liquor to the absorber) was tested only at the low inlet SO_2 levels of Period 1. With just the venturi, 95% SO_2 removal efficiency (less than 50 ppm outlet SO_2) required a bleed liquor pH of about 6.5. However, better than 90% removal could still be quite easily achieved at pH's on the order of 6.0. When the venturi alone was used, the bleed liquor pH was generally maintained above 5.7 to keep outlet SO_2 levels at or below 100 ppm.

Appendix F contains estimates of the stage efficiencies in the scrubber system. The analysis is based upon operation with both the absorber and venturi during stable periods at high and low inlet SO_2 levels.

j. Lime Utilization

Lime utilization throughout all three operating periods was quite good. Under normal conditions, lime utilization ranged from 90% to 100% of the available $Ca(OH)_2$ in the raw, hydrated lime, and typically ran about 94%. The $Ca(OH)_2$ fraction of the delivered lime ranged from 87% to 91% (wt % basis).

Table V-7 summarizes the estimates of lime utilization and overall lime/ΔSO_2 feed stoichiometry for balance intervals during each of the three operating periods. Feed stoichiometries are calculated from integral average SO_2 removal rates, and from lime deliveries and lime silo inventories. Lime utilization estimates have been calculated by two methods -- first, from the analyses of the filter cake solids; and second, from the overall feed stoichiometry taking into account sodium carbonate feed (and sodium-sulfur losses). The small differences between the two different estimates of utilization indicate the closure of the material balance. And the difference between the lime feed stoichiometry and unity reflects both utilization and soda ash makeup. Lower lime utilization increases the stoichiometry, tending toward values greater than unity; higher soda ash feed rates decrease the stoichiometry, tending to reduce stoichiometry below unity.

Accurate estimates of lime/ΔSO_2 stoichiometry are not possible for extended, uninterrupted intervals during operating Period 1. The outlet SO_2 monitoring was not operational until April 1975, and accurate accounting of lime deliveries and silo inventories was not initiated until June 1975, when the filter cake weigh scales were installed. In addition, there were frequent periods when unknown quantities of limestone were inadvertently charged to the lime silo. Therefore, estimates of lime utilization from filter cake analyses during periods when little or no limestone contaminated the lime supply have been used to back-calculate lime feed stoichiometry.

TABLE V-7

LIME UTILIZATION DURING STABLE LOAD OPERATION

Period	Balance Interval	Coal Fired	Approximate Duration of Balance Period (Hours)	Lime Feed Stoichiometry ($Ca(OH)_2/SO_2$)	Lime Utilization (% of $Ca(OH)_2$)	
					From Lime Feed Stoichiometry	Filter Cake Analysis
1	4 - 6/75	Low-Sulfur	(1,300)	(~41.95)	-	(92-98)
2	11/3 - 11/23/75	Low/Medium-Sulfur	1,050	0.95	96.0	96.5
3	4/11 - 5/23/76	High-Sulfur	940	1.085	91.0	93.0

In Period 4, detailed material balances were computed for the last two months -- November and December 1975. The overall lime/ΔSO_2 feed stoichiometry of 0.95 and lime utilization of 96-97% (based upon available $Ca(OH)_2$) are representative of the entire three and one-half months of Period 3.

The balance interval for Period 3 covers the five-week period beginning the second week of April when stable system chemistry was achieved and ending in May just prior to starting the fluctuating load testing. The closeness of the lime utilization estimates calculated both from the overall lime/ΔSO_2 stoichiometry and from the analyses of filter cake samples reflects the accuracy of the material balance during this period. The slightly lower utilizations estimated for Period 3 with the high-sulfur coal (93%) versus that for Period 2 with the mixed low- and medium-sulfur coal (~96%) does not represent any basic change in the system chemistry or capability of the technology. In fact, utilization would be expected to improve with higher sulfur content in the coal due to lower soluble sulfate concentrations (lower system oxidation rates). The slightly lower utilization figures for Period 3 can be attributed to two factors: first, the average extent of regeneration (pH) during Period 3 (pH = 11.5-12.3) was slightly higher than in Period 2 (pH = 11-12); second, the reactor holdup time during Period 3 ranged from 20-30 minutes and averaged about 30 minutes, while during Period 2, the average holdup time was longer, averaging closer to 40-45 minutes. The shorter holdup time in Period 3 (due to higher liquor rates with the higher-sulfur coal) in combination with the slightly higher operating pH would have a tendency to depress lime utilization slightly. The higher chloride content (0.25-0.35M Cl^- in Period 3 versus 0.03-0.06M in Period 2) may also have had a minor effect, although prior work at ADL has not shown any significant difference due to chloride at these concentrations.

It is worth noting that during Periods 1 and 2, lime was fed to the reactor system only as a dry solid, while in Period 3, lime was fed at different times as a dry solid or as a slurry containing from 12% to 33% solids. There was no discernible effect of the difference in the form of lime feed during Period 3.

4. Oxidation and Sulfate Control

a. Oxidation

As would be expected, the major portion of the sulfite oxidation in the system occurred in the scrubber circuit, and the single most important variable affecting the oxidation rate was the oxygen content of the flue gas. Estimated oxidation rates in the scrubber circuit ranged from a low of about 150 ppm equivalent SO_2 (at 4.5-5.0% oxygen in the flue gas) to as high as 450 ppm (at oxygen levels up to 9-10%). By contrast, oxidation throughout the remainder of the process is estimated to have been 25-40 ppm. Thus, in general, oxidation in the scrubber circuit accounted for more than 85% of the total system oxidation.

Figures V-4 and V-5 are plots of estimated oxidation rates in the scrubber system in equivalent ppm of SO_2 (design gas flow basis) as a function of oxygen content of the flue gas. Design gas flow is used as a normalizing factor since oxidation was not significantly affected by small changes in gas flow.

Data in Figure V-4 cover operation with mixed low- and medium-sulfur coals and both scrubber configurations used during Periods 1 and 2. Figure V-5 shows data with high-sulfur coal operation during Period 3 using the venturi/two-tray combination. The data shown were screened to ensure relatively stable operation (gas flow and oxygen content, and liquor flow and composition) to minimize random data scatter.

It would be expected that oxidation rates would be somewhat lower using the venturi alone than with the combined venturi and absorber, due to the decreased gas/liquid contacting. However, such a decrease in oxidation is not apparent in Figure V-4. This can be attributed to three factors: first, the carryover of entrained liquor from the venturi to the absorber; second, contacting of gas with liquor recirculated through the open spray header; and finally, the flow of a small amount of regenerated liquor onto the top tray through a leaky shutoff valve.

Considering all data regardless of scrubber configuration, the data scatter exhibited in Figure V-4 amounts to a range of 80 ppm of oxidation at a given flue gas oxygen level. This data scatter can be accounted for by differences in operating temperature (120-135°F), liquor flow, slight differences in pressure drop, and error in the oxygen analyzer, as well as sampling and analytical errors.

Assuming that the median value of oxidation represents the average oxidation experienced, then oxidation in Periods 1 and 2 ranged from 175 ± 40 ppm at 3% oxygen to 180 ± 40 ppm at 9% oxygen. For a typical SO_2 level of 1,200 ppm with 95% SO_2 removal and 90% gas load, these oxidation rates correspond to 17% and 17% of the SO_2 removed, respectively. Adding in the oxidation through the remainder of the system, the total oxidation amounted to 20% of the SO_2 removed at a 3% oxygen level and 40% at 9% oxygen. It should be noted that these oxidation rates represent operation with three active contact stages (apparently even when the venturi was operated alone). Normally in a low- or medium-sulfur coal application only one, or at most, two stages should be required. This reduction in the number of stages would significantly reduce oxidation rates.

The oxidation data plotted in Figure V-5 for high-sulfur coal operation show an increase of about one-third in oxidation over that observed with the lower-sulfur coals. However, as a percentage of the SO_2 absorbed, there is a significant decrease owing to the higher inlet SO_2. At a 6% oxygen level the estimated median oxidation rate with high-sulfur coal in Period 3 was about 270 ppm of SO_2 (~13% of the SO_2 removed), compared with 210 ppm operating with the mixed low- and medium-sulfur coals in Periods 1 and 2 (20-25% of the SO_2 removed). At 8% oxygen the estimated average oxidation rate in Period 3 was about 430 ppm of SO_2 (~21% of the

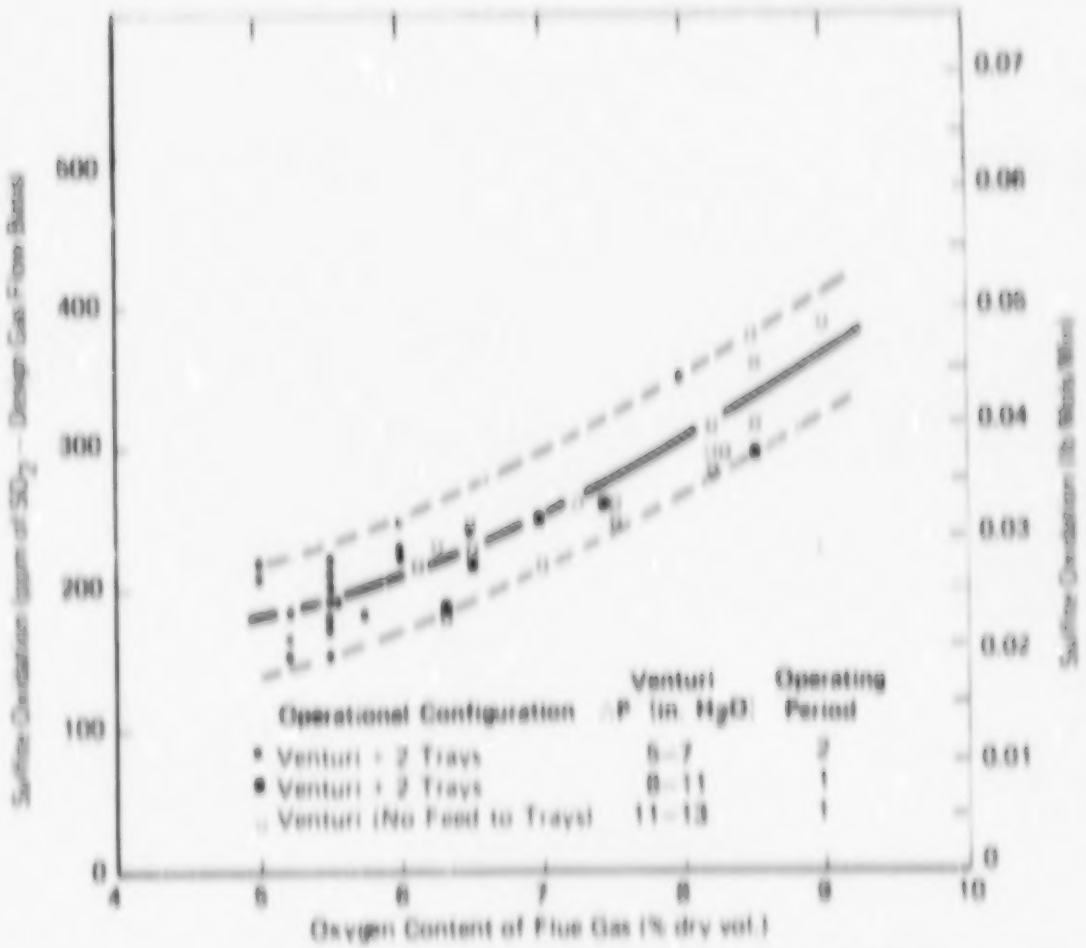


FIGURE V-4 OXIDATION IN THE SCRUBBER SYSTEM AS A FUNCTION OF FLUE GAS OXYGEN CONTENT (PERIODS 1 AND 2)

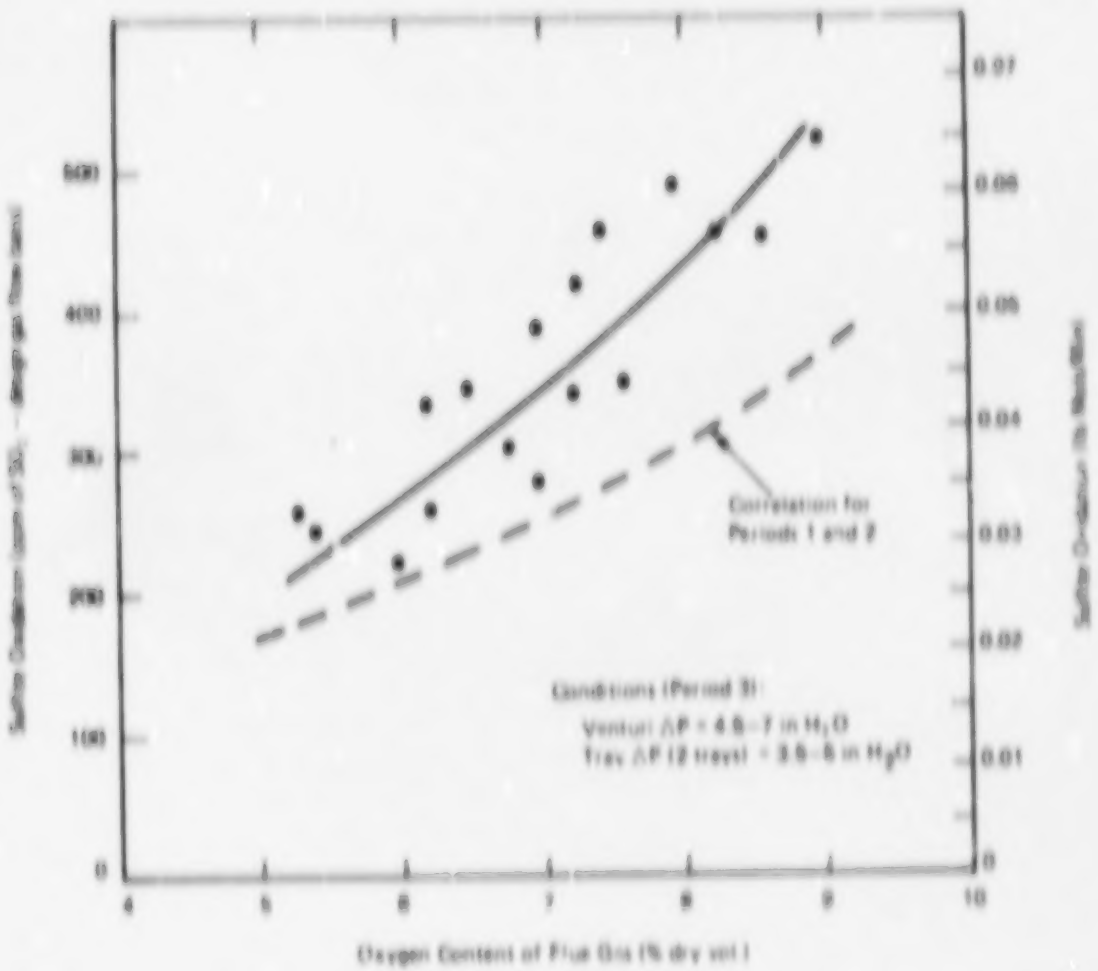


FIGURE V-6 OXIDATION IN THE SCRUBBER SYSTEM AS A FUNCTION OF FLUE GAS OXYGEN CONTENT (PERIOD 3)

SO_2 removed), compared with 310 ppm in Periods 1 and 2 (29-37% of the ΔSO_2 removed). This increase in the absolute oxidation rate in Period 3 is not readily explainable. It may have been due, in part, to the higher active sodium levels (0.25-0.35M Na^+_{active} in Period 2 versus 0.35 to 0.45M Na^+_{active} in Period 3). This would be a factor if oxidation were partly reaction rate limited. Subtle differences in trace contaminants in the flue gas due to differences in coals may also have played a part. The oxidation of sulfite is known to be sensitive to the catalytic effects of trace levels of heavy metals and inhibitory effects of certain organics.

It is important to note, though, that the oxidation levels experienced in Period 3 are well within the range that can be handled by the system capability for sulfate precipitation.

b. Sulfate Precipitation

At steady state, the total sulfate being formed must be removed from the system at an equivalent rate by the precipitation of calcium sulfate and attendant sodium sulfate losses in the filter cake. Calcium sulfate levels measured in the product solids ranged from as low as a few percent of the total insoluble calcium-sulfur salts (during early startup) to as high as 90% during periods of high oxygen levels and low inlet SO_2 (when the ratio of sodium sulfate to active sodium in the system liquor was fairly high). The typical range of calcium sulfate in the waste cake during Period 1 was 15% to 25% (wet basis) of the total calcium-sulfur salts; in Period 2, calcium sulfate in the cake ranged from 12% to 20%; and in Period 3, the calcium sulfate fraction in the cake ranged from 6% to 17%.

These levels of calcium sulfate precipitation indicate that the system is capable of keeping up with oxidation rates of up to 25-30% of the SO_2 removal in the concentrated mode of operation without excessive sodium losses. In operations where the cake is thoroughly washed, essentially all of the sulfate losses would be as calcium sulfate. Sodium sulfate losses, which usually amount to 50-60% of the total sodium value occluded in the cake, would represent less than 2% of the SO_2 absorbed. Depending upon the levels of oxidation experienced and the degree of cake washing, the system liquor composition would simply readjust so that the ratio of sodium sulfate to active sodium would allow precipitation of the amount of calcium sulfate required to keep up with oxidation.

Figure V-6 shows the relationship between the ratio of calcium sulfate to calcium sulfite in the waste solids versus the ratio of soluble sulfate to sulfite in the regenerated liquor. The data plotted are taken from stable operating periods lasting at least a few days. The dashed line represents the relationship derived from the pilot plant operations for calcium sulfate in the reactor effluent solids. The data for the calcium sulfate content of the reactor effluent solids in the prototype system are slightly displaced from the pilot plant correlation. Based upon the data shown in Figure V-6, the correlation of the sulfate/sulfite content of the precipitated calcium salts to the sulfate/sulfite concentrations

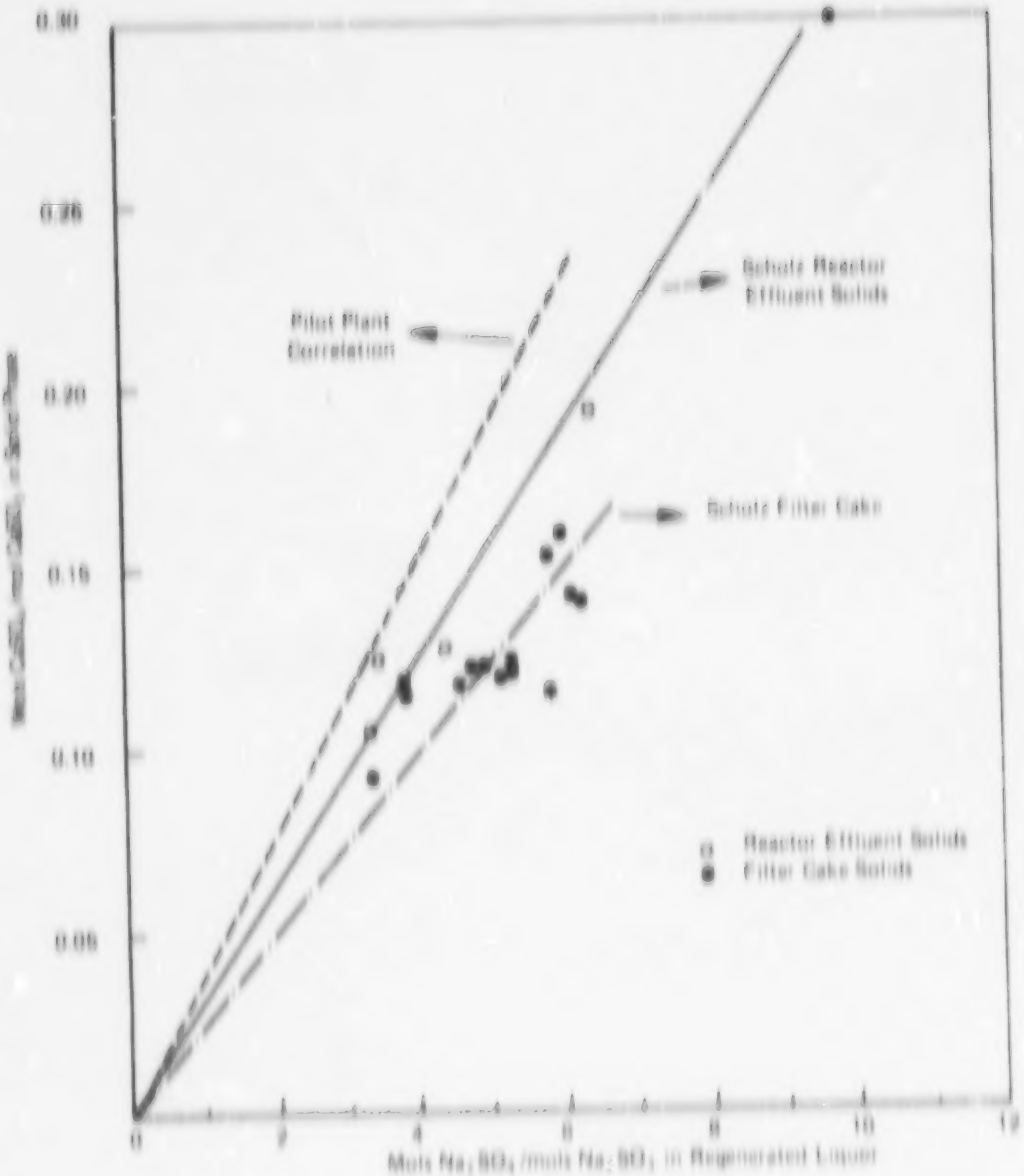


FIGURE V-6 $(Ca(SO_3)_2/CaSO_4)$ RATIO IN WASTE SOLIDS AS A FUNCTION OF (Na_2CO_3/Na_2SO_3) RATIO IN REGENERATED LIQUOR

in the reactor liquor can be approximated by the following relationship:

$$\left(\frac{\text{mols } CaSO_4}{\text{mols } CaSO_3}\right)_{\text{reactor solids}} = 0.031 \left(\frac{[SO_4^=]}{[SO_3^=]}\right)_{\text{reactor liquor}} \qquad (1)$$

This level of sulfate precipitation is about 85% of that observed in the pilot plant operations.

There was a small, but significant decrease in the calcium sulfate in the filter cake compared with that in the reactor solids. This corroborates previous laboratory results indicating that a small amount of calcium sulfate apparently does redissolve on prolonged contact with the regenerated liquor. The redissolution of calcium sulfate amounted to an average of about 13% of the total calcium sulfate originally precipitated. This was determined during a particularly stable two-week interval in Period 3 when the $CaSO_4/CaSO_x$ mol ratio in the reactor solids averaged 11.7% ($CaSO_4/CaSO_3$ = 0.132) and the filter cake contained a $CaSO_4/CaSO_x$ mol ratio of 10.1% ($CaSO_4/CaSO_3$ = 0.112). This differential corresponds to a decrease of 13.5% in calcium sulfate. A small portion of the decrease is due to continued reaction and precipitation of calcium sulfite at the higher reactor operating pH's. The data shown in Figure V-6 suggests about a 15% drop in calcium sulfate in the cake from that in the reactor effluent solids.

Sulfate balances were performed over three separate intervals in Periods 2 and 3, each lasting three to five weeks. Table V-8 summarizes these balances. The estimated total system oxidation shown is the sum of the oxidation in the scrubber system (based upon the average flue gas oxygen content over the interval) and in the combined reactor/dewatering systems. The sulfate account is based upon the average filter cake analyses and total cake discharged, sodium inventory in the liquor and the total soda ash fed.

In all cases the relative error in the sulfate balance (difference between sulfate formation and sulfate account) is less than 10%. While this alone does not guarantee a high degree of accuracy in the various estimates of oxidation, soda ash feed, and calcium sulfate precipitation, it does indicate that overall the material balances are substantially correct.

During November, 20% of the SO_2 absorbed was oxidized to sulfate. Of this, 13% left the system as insoluble calcium sulfate. The remaining 7% (as calculated from the total soda ash feed and the composition of the system liquor) left as sodium sulfate. Based upon analyses of filter cake samples, about half of the sodium sulfate was lost from the system in the liquor occluded in the filter cake (0.5% sodium salts on a dry cake basis). The other half of the sodium sulfate losses are unaccounted for. Leaks from pump seals and tanks, and entrainment losses (which are discussed later) were all quite small and realistically could only amount to, at most, half of the unaccounted for losses. The remaining 2-3% of

TABLE V-8

SYSTEM SULFATE BALANCES

	PERIOD 2		PERIOD 1
	11/3-11/23/75	12/2-12/23/75	5/11-5/23/75
Average Inlet SO_2 (ppm)	1,265	1,135	2,115
Average SO_2 Removal (%)	95.5	96.5	96.4
Average Inlet O_2 (vol. %)	5.5	6.0	6.5
Total Sulfate Formation (ΔSO_4)	20.0	21.0	17.5
Sulfate Account ($\Sigma \Delta SO_4$):			
In Cake - $CaSO_4$	13.0	15.0	10.5
Na_2SO_4	4.5	3.0	5.0
Na_2SO_4 in System Liquor Inventory[a]	-0.5	2.5	0.0
Other[b]	4.0	1.0	1.5
Total	21.0	21.5	17.0

[a] A negative value represents a decrease in sulfate concentration in the system liquor over the balance interval.

[b] Other represents the sodium sulfate losses from the system that are not accounted for by cake losses and changes in sodium sulfate inventory (accumulation or depletion) in the system liquor. Other includes sulfate losses from pump seal leaks and inadvertent spills and is calculated independently of the total sulfate balance from the soda ash makeup rate and the average solution chemistry, as follows:

$$\text{Other} = \text{Soda Ash Makeup} \times \left(\frac{\text{Average solution sulfate concentration}}{\text{Average total } Na_2^{++} \text{ concentration}} \right)$$

$$- \text{ sodium sulfate losses in the cake - accumulation of sodium sulfate in the system liquor}$$

Since the estimate is based upon the soda ash makeup, it inherently includes any errors in the estimate of the soda ash feed.

the sodium losses, therefore, may be due to unreported spills or, more likely, to inaccuracies in the estimates of soda ash makeup and poor washing of the filter cake during some periods when it was not sampled.

In December, due to the slightly higher average oxygen content of the flue gas and the slightly lower inlet SO_2 levels, 73% of the SO_2 absorbed was oxidized to sulfate. About 15% left the system as insoluble calcium sulfate in the filter cake; the remainder was accounted for by sodium sulfate losses based upon the total soda ash feed. The losses included 8% as sodium sulfate in the filter cake (0.5% sodium salts - dry cake weight); 3.5% sodium sulfate accumulation in the liquor inventory; with, again, 3% unaccounted for. Because of the relatively large unaccounted for sodium losses during Period 3, attempts were made during the third balance interval (in Period 3) to ensure good, representative cake sampling and minimize (or report accurately) spills and leaks.

With the high-sulfur coal in Period 3 and oxygen concentrations ranging from 5.5% to 9% in the flue gas (averaging about 6.5%), total system oxidation averaged about 17.5% over the five-week material balance interval. The calcium sulfate fraction of the filter cake averaged 10.5% of the ΔSO_2 and sodium sulfate in the cake averaged about 5.0% of the ΔSO_2. Other losses of sodium sulfate as calculated from the total soda ash makeup amounted to 1.5% of the ΔSO_2. Of this 1.5%, approximately 0.25% is estimated to have resulted from known spills (0.2%) and entrainment losses (0.05%). The remaining 1.25% is unaccounted for and represents pump seal and piping leaks; unreported spills; and perhaps most importantly errors in the estimate of the total soda ash makeup, and errors in cake loss estimates. This 1.25% discrepancy is much lower than the discrepancy in Period 2 and reflects the efforts made to control and monitor the sodium balance.

If all system leaks had been stopped or returned to the system and the cake had been washed to the same level of soluble solids, then the sulfate-to-active-sodium ratio in the liquor would have increased slightly (as shown in Figure V-6) to allow more calcium sulfate to precipitate, thereby re-establishing the equilibrium between sulfate formation and losses.

5. Waste Cake Properties

a. Solids Content

The solids content of the filter cake produced throughout the program typically ranged from 45% to 60% solids. However, over all operating conditions encountered during the 17 months, filter cakes containing as high as 71% and as low as 41% solids were produced. For the most part, during normal filter operation, the filter cake had the consistency and handling properties of a moist powder, as shown in the photographs in Figures V-7 and V-8. Table V-9 summarizes the filter cake properties during each stable load period.

FIGURE 7-1 ELEVATION-MAINTENANCE SIDE

[illegible]

TABLE 1-A

SUMMARY OF FILTER CAKE PROPERTIES

Operating Period	1		2		3	
	Range (2-7/75)	Average (5-6/75)	Range (9-12/75)	Average (11-12/75)	Range (3-5/76)	Average (4-5/76)
Coal Sulfur Content (wt %)	0.8-2.2	1.6	1.5-3.1	2.1	2.4-5.1	3.7
Filter Cake Properties:						
Solids Content (%)	41-77	48[a]	45-71	52[a]	49-62	54[a]
$CaSO_3/CaSO_3$ (mol ratio)	<0.02-0.31	(0.17)[c]	0.09-0.17	0.15	0.05-0.14	0.11
Solubles (wt % dry cake)	—	(8)[c]	—	4	—	5
No. Displacement Washes	—	(0.5-1)[d]	—	2	—	1.6
No. of Spray Banks	—	2	—	3	—	3[a]

a Includes intervals of limestone contamination of lime supply.
b Includes intervals of filter testing (drum speed, filter cloth, wash spray).
c Estimated based upon analyses of 4 to 12 cake samples.
d Estimated from available wash spray data.

In general, solids content (and, therefore, cake quality) was a function of three factors:

- normal variations in process chemistry -- principally the level of calcium sulfate in the waste solids;
- filter operating variables -- principally drum speed and type of filter cloth, both of which were varied during the program; and
- system upsets -- including process upsets such as contamination of the lime feed supply with limestone and gross overfeeding of lime, as well as mechanical problems with the filter which affected the filter performance or with the reactor system which affected solids properties (see Section V.E., MECHANICAL PERFORMANCE).

Data shown in Table V-9 include all of these effects for the operating intervals reported.

Most system upsets, both process and mechanical, occurred during the first operating period. While these upsets sometimes reduced solids content of the filter cake by as much as 5-10%, for the most part they were discrete incidents with identifiable causes (e.g., limestone contamination of lime, cracking of plastic support grids in filter, etc.) peculiar to the Scholz operation and with little significance to full-scale applications. The two most important upsets in terms of effects on filter cake properties were the presence of large quantities of limestone in the lime feed supply and the mechanical problems with the filter that reduced filter vacuum. During Periods 2 and 3 there was only one incident of limestone contamination and there were few mechanical failures in the filtration system.

While the data in Table V-9 include upset conditions, the general effect of the level of sulfate content of the cake (or system oxidation) is apparent. As sulfate precipitation (oxidation) increased, the solids content of the filter cake decreased. Although the effect is small, it is real and confirms a similar trend observed in the pilot plant operations (see Volume II). A quantitative correlation of filter cake solids content with either calcium sulfate fraction or soluble sulfate-to-TDS ratio similar to that developed from pilot plant operations is not possible, though, due to the fluctuations in operating conditions and variations in filter vacuum resulting from filter mechanical problems and filter testing.

b. Solubles

Wash efficiency tests conducted at Scholz during Period 1 demonstrated that the soluble solids content of the cake could be readily reduced to 2-3% (dry cake basis) under controlled conditions using a wash ratio of about 2.5 (gals wash water/gal water occluded in the cake). These tests were performed using two spray banks in series. Two banks provided sufficient water to achieve a wash ratio of up to 4 at the low cake

discharge rates normally experienced with the low-sulfur coal in Period 1. However, mechanical problems and improper filter operation frequently prevented a reasonably continuous operation of the filter with a thin enough cake to allow consistently high wash ratios (> 1.5) required for low solubles losses. There were also periods when the cake was not washed. In Period 1, the levels of solubles in the filter cake ranged from 2% to 12% (dry cake basis) and typically ranged from 5% to 8%. The 12% solubles occurred during periods when the cake was not washed.

In order to increase the available wash water for periods of high solids withdrawal, a third bank of spray nozzles was added to the filter prior to the start of the second operating period. Then, following the first month of operation in Period 2, the capacity of the sprays was increased. These adjustments roughly doubled the total wash capacity from 3-3.5 gpm to 7 gpm. As a result, in November 1975, the level of soluble solids in the cake averaged 4.8% (dry cake basis) with a wash ratio of 1.5-2.0. In December, the wash rate was increased to a wash ratio of 2.0-2.5 and the average soluble solids level in December decreased to 3.3% (a range of 1.5% to 6.0% dry cake basis). The solids content of the filter cake during both months averaged 51%.

In anticipation of higher solids production rates during higher-sulfur coal testing in Period 3, a fourth bank of high capacity sprays was added to the filter during the interim between Periods 2 and 3. This resulted in a further increase in the wash capacity from 7 gpm to about 10 gpm. Some difficulty was experienced with the higher capacity nozzles. The high water velocities from these full-cone nozzles tended to wash cake off the cloth, which contributed to cloth blinding. These nozzles were later replaced and total wash capacity reduced to 8-9 gpm. Improved mechanical performance of the filter following overhaul, though, did allow a fairly continuous operation of the filter and wash ratios were typically maintained between 1.5 and 2.0. The average wash ratio during April and May, as calculated from total cake discharged and total wash water fed, was about 1.9. The average solubles loss in the cake with this wash rate was 5% (dry cake basis). The range of soluble levels experienced ran from 1.3% to a high of 11.5% (very little washing).

As in other periods of operation, the solubles content of the cake varied with cake thickness. Even during stable, continuous operation, differences in cake thickness across the filter resulted in a range of sodium in the cake discharged from different points of the filter. Typically, the cake at the ends of the drum (6-8" on each end) ran about twice the thickness of the cake in the middle of the drum and usually contained 1.5 to 2 times the solubles levels. This difference in cake thickness was accounted for by taking a mixed sample of different thicknesses or taking what appeared to be the average cake thickness. Occasionally, a number of samples from across the cloth were taken as a check.

c. Filter Testing

Filter testing was conducted at Scholz both on the Dorr-Oliver vacuum drum filter and on a pilot-scale rotary drum vacuum filter supplied by the Bird Machine Company. The filter testing performed with the Dorr-Oliver unit, over and above that related to solving mechanical problems, involved the evaluation of different filter cloths, and general optimization of filter control (drum speed, wash efficiency, feed slurry concentrations, etc.).

The filter cloth testing began midway through the first operating period and continued throughout the remainder of the program. The purpose of the testing was to minimize or eliminate blinding and increase cloth life without sacrificing high cake solids content or filtrate clarity. A number of different nylon, polyester, and polypropylene cloths in both monofilament and multifilament weaves were tested. Porosities of the cloths tested ranged from 10 cfm to 100 cfm (air flow per square foot of cloth measured at a pressure drop of 1/2 inch of water). Overall, the polypropylene monofilament with a porosity of 20-30 cfm was found to be most suitable. The cake release was very good and the filtrate clarity was excellent (at most, a few hundred ppm of suspended solids). Depending upon the care taken during installation and operation, this cloth had a life up to a month or more. Based upon this experience, a projected life of at least a few months on a full-scale system would be reasonable. The multifilament, simply because of the greater strength imparted by the weave, was more durable but tended to blind more readily (requiring cleaning of the cloth two to three times per week). Nylon was not acceptable at Scholz due to the occasional excursions to low pH.

Testing with the Bird filter was performed during May and June 1976. While the Bird filter design was significantly different from that of the Dorr-Oliver filter, the performance was roughly equivalent in terms of filtration rate, dewatering capability, and wash efficiency. There was a slightly higher carry-through of solids into the filtrate which has been attributed to the thinner cake with the Bird filter. The thinner cake allows more fines to be pulled through the cloth. Sufficient time was not available, though, to optimize the Bird filter fully, particularly with regard to the type of cloth.

6. Sodium Makeup

The sodium makeup requirement in the operation of a dual alkali system is determined simply by the rate of sodium loss, both controlled (solubles in the filter cake) and uncontrolled (pump seal leaks, tank spills, etc.). Under normal operating conditions in a tight, closed-loop operation the losses in the filter cake are the single most important sodium loss, and sodium makeup should equal or only slightly exceed the quantity contained in the cake (on a mol equivalent basis).

As previously indicated, wash efficiency tests performed at Scholz during Period 1 showed that 2-3% solubles losses in the cake (weight %, dry cake basis) could be easily achieved with a wash ratio of 2.5, and that solids contents as low as 1.5% could be attained at slightly higher wash ratios. Solubles losses of about 1.5% probably represent a reasonable lower limit for continuous operation because of limitations in water balance and the need to purge chlorides at the rate at which they enter the system. These solubles losses translate almost directly into an equivalent soda ash makeup requirement because of similarities in molecular weights of the sodium and calcium-sulfur salts. A 1.5% solubles loss usually corresponds to a soda ash makeup requirement of between 1.5% and 2.0% of the SO_2 absorbed (mols Na_2CO_3/mol ΔSO_2). Soda ash makeup to the system was consistently higher than this lower level throughout the operation.

During Period 1, mechanical problems with the filter and insufficient washing limited the level to which soluble sodium salts could be washed from the cake over an extended period to a minimum of about 5%. In addition to the cake losses, there were also inadvertent spills as new operators gained familiarity with the system, as well as the normal leaks from pump packing, piping, etc. Thus, soda ash makeup requirements frequently exceeded 10% of the SO_2 absorbed on a mol basis during Period 1.

The improvements in the filter operation and increased wash efficiency in Period 2 substantially reduced sodium losses in the cake to 4.8% solubles in November 1975 and 3.3% solubles in December. These sodium losses correspond to soda ash makeup requirements equivalent to 5.8% and 3.6% of the SO_2 absorbed, respectively. The net soda ash makeup (not including that used in increasing the inventory of sodium in the system), however, was 10.5% in November and 7% in December. The higher makeup requirement in November was partially due to contamination of the lime with 25 tons of limestone, decreasing the washability of the waste and increasing the amount of waste solids and associated sodium losses.

The apparent difference of 3-4% between the estimated soda ash feed and sodium losses in the cake during November and December can be attributed to leakage from the system, errors in estimates of the soda ash feed, and sampling error in the cake. Very few samples were taken during evening shifts when there was a greater tendency for improper filter operation, including poorer washing.

Entrainment losses of sodium were very small. In particulate sampling conducted during December (by Guardian Testing Services), the total weight of sodium salts in the scrubbed gas averaged 0.002 grains/scf. This represents a liquor loss through entrainment of less than one gallon per hour. The soda ash makeup required to replace this entrainment loss is less than 0.1 mol % of the SO_2 absorbed. Additional gas sampling performed during Period 3 (June-July 1976) showed even lower entrainment losses of sodium than measured during the Guardian testing (see Section V.D, PROCESS PERFORMANCE - PARTICULATE TESTING).

Because of the inability to close the sodium balance during Period 2, efforts were made to minimize the potential for accidental spills and leaks during Period 3, and to monitor soda ash makeup, cake losses and cake washing more accurately. As an aid in monitoring cake wash water, a wash water totalizer was installed prior to Period 3.

Analyses of cake samples throughout April and May (in Period 3) indicated a solubles loss in the cake averaging about 5% of the total dry cake weight. Based upon total cake withdrawn from the system, this corresponded to a soda ash makeup requirement of about 7.0% of the SO_2 absorbed (moles Na_2CO_3/100 moles ASO_2) or a requirement which was about 0.5-1.0% higher than normally expected due to the high quantity of waste solids withdrawn compared to SO_2 removed. The higher estimated cake rate in part can be attributed to a higher lime feed stoichiometry in Period 3 (slightly decreased utilization as previously discussed) and the low available $Ca(OH)_2$ in the lime; but it also reflects errors in estimates of SO_2 absorbed, in recorded cake weights, and small errors introduced in data averaging.

Despite these errors, the 7.0% is still quite close to the net soda ash makeup rate of 8.0% of the SO_2 absorbed estimated for April and May. As in Period 2 the difference of 1.0% cannot be explained by pump seal leaks and known (small) spills; rather this difference reflects errors in cake sampling and inadequate washing of the cake during periods when the cake was not sampled (evenings and filter startup and shutdown). The tendency in the filter operation was to underwash the cake and for wide fluctuations in wash ratios. While the average wash ratio may have been 1.8, extended operation at a wash ratio of 1.0 would require an equivalent period of operation with a wash ratio of about 3 to result in the same total sodium losses as with a steady wash ratio of 1.8. This effect is signified by the fact that most periods of higher wash ratio were when less cake was being discharged.

Problems of inadequate washing can be avoided to a great degree in larger systems simply through the use of multiple filters which would normally be required. A multiple filter system would not allow one filter to run alternately starved and overloaded. And interlock controls on wash water and filter operation would reduce the tendency to underwash the cake.

7. Process Operability

Process operability refers to the overall ease of process operation, including the resistance of the process chemistry to operational upsets, the sensitivity of the process performance to small changes in the process chemistry, and the potential for scaling in the process equipment. In this regard, it is to be differentiated from the mechanical/equipment-related problems previously discussed.

In all respects the process operability was excellent. The system was successfully operated over a range of widely fluctuating inlet SO_2 levels and flue gas oxygen concentrations during each period of testing with

little or no change in the SO_2 removal efficiency, cake properties, or lime utilization. The system demonstrated an ability for continuous operation with large and frequent variations in pH in both the scrubber circuit (pH = 4-7) and regeneration/dewatering section (pH = 8.5-13). And the low soluble calcium levels throughout the system even during most upset conditions resulted in a low potential for scale formation, particularly in the scrubber circuit. During Period 1 with active sodium concentrations between 0.15M and 0.30M, soluble calcium levels generally fluctuated between 20 ppm and 250 ppm and were usually less than 150 ppm. In Periods 2 and 3, when active sodium levels were maintained above 0.3M, soluble calcium concentrations typically ran about 70 ppm and were consistently below 100 ppm. The low potential for scale formation or solids deposition in the scrubber was further demonstrated in Periods 2 and 3, when operation of the wash sprays on the demister was discontinued. During the last three months of Period 2 and throughout Period 3 (including particulate testing) the wash sprays were not used. Inspection of the demister after Period 2 and following completion of the test program showed the demister to be free of scale or deposit of any kind -- after about 4,500 hours of operation.

There were only two problems with scale formation/deposition of solids in the system. First, there was a continuous, slow buildup of solids in the small first reactor during all periods of operation. This problem was closely linked to major upsets in the lime feed and reactor agitation and is discussed later as a part of equipment performance. At worst, such buildup if it were to occur would be expected to require quarterly or semiannual cleaning as a part of a regular maintenance program. In a full-scale system the cleaning would not require a shutdown of the system, since flow could be switched to another reactor train or the first reactor bypassed.

Second, there was precipitation and deposition of gypsum scale in the reactor vessels and reactor outlet piping in July 1975 (Period 1). This resulted from a simultaneous drop in inlet SO_2 levels to 850-950 ppm and an increase in flue gas oxygen levels to 8.5-10% -- a condition which persisted for several days. The system was allowed to drift into a dilute mode of operation (active sodium levels decreased to below 0.15M) and the low soluble sulfite concentrations resulted in calcium supersaturation with respect to gypsum. While this did not cause a shutdown of the system, the scale in the piping did reduce the feed forward capacity by about 20%. Most of the gypsum scale was removed during the interim between Periods 1 and 2. A second parallel (polybutylene) pipeline was also installed between Periods 2 and 3 to ensure sufficient feed forward capacity for high-sulfur coal testing.

In addition to the fluctuating SO_2 levels and oxygen concentrations, the system also experienced a number of process upsets during stable load testing. These upsets included the carryover of small amounts of fly ash (Period 1), the contamination of the lime feed supply with limestone (Periods 1 and 2), and occasional overfeeding of lime (all periods). Only the limestone had any significant effect on the process performance and

this effect was temporary. During periods when pure limestone was fed to the reactor system, the pH of the regenerated liquor fell to below 7, causing a loss of SO_2 removal efficiency, from above 90% down to 80-85%. The solids content of the filter cake also decreased slightly and sodium losses in the cake correspondingly increased. Within a day or two after the limestone had passed through the system, all of the effects were reversed and the system operation returned to normal.

C. PROCESS PERFORMANCE -- FLUCTUATING LOAD

Following completion of the stable load testing on high-sulfur coal in May 1978, the system was operated with a fluctuating gas load for a period of two weeks (5/1-5/14/78). The purpose of this testing was to evaluate the effects of regular wide swings in gas flow (boiler load) on system performance. While the gas flow to the system had been curtailed to as low as 30% of design capacity for brief periods during stable load operation, prior to fluctuating load testing there was no attempt to follow or simulate swings in boiler load.

There were three primary objectives of fluctuating load testing: first, to determine the effect of the changes in gas flow on SO_2 removal efficiency; second, to evaluate the operability of the system both during load changes and overall (as a result of the fluctuating conditions); and finally, to determine the effect of fluctuating load conditions on the system chemistry and process performance.

During fluctuating load testing, gas flow to the system was regularly adjusted to four different levels between 30% and 100% of design load according to a prearranged schedule roughly representative of the normal operation of the Schols boilers. The gas load schedule used is shown in Figure V-9. The average gas rate to the system corresponded to about 65% of design load.

During fluctuating load testing, inlet SO_2 levels ranged from 1,550 ppm to 2,700 ppm and averaged about 2,100 ppm. Oxygen levels in the flue gas varied from 5.5% to 9.0% and typically ran about 7.5%. The pressure drop across the venturi throat was maintained between 6 and 7 inches of water (average of about 5 inches of water) to ensure saturation of the gas. The pressure drop across the two trays and demister varied with gas load from a low of 2.2 inches of water to a high of about 6.7 inches of water. Liquor recirculation rates about the venturi and tray absorber were maintained essentially constant at the different gas rates for convenience. Total liquor feed to the tray tower, therefore, ranged from an L/G of about 7 (at 100% load) to 9 (at 30% load). Similarly, the venturi L/G ranged from about 20 to about 60. Table V-10 summarizes the operating conditions.

Overall, the system performance during fluctuating load testing was excellent. There were no problems of scale formation, decreased SO_2 removal efficiency or deterioration of reactor performance. Table V-11 summarizes

TABLE 1-10

SUMMARY OF SYSTEM OPERATING CONDITIONS
FLUCTUATING LOAD TESTING
(6/1-6/14/76)

	Range	Average
Inlet Flue Gas:		
Flue Gas Rate, (equiv. No.)	6-20	13
(% of design load)	30-100	65
SO_2 Level, (ppm)	1,650-2,600	2,150
O_2 Concentration, (vol. %)	5.5-8.0	7.5
Temperature, (°F)	290-305	~315
Fly ash, (grains/scf dry)	<0.03	—
Venturi Scrubber:		
Pressure Drop, (inches of water)	4-7	5
Liquor Recirculation Rate, (L/G - gals./Mscf)[a]	30-60	40
Tray Tower (Absorber):		
Pressure Drop, (inches of water)	2.2-4.7	3.5
Liquor Recirculation Rate, (L/G - gals./Mscf)[a]	5-9	7

[a]Liquor recirculation rates were not adjusted during fluctuating load testing.

TABLE V-11

COMPARATIVE PERFORMANCE CHARACTERISTICS
STABLE VS FLUCTUATING LOAD

	Stable Load (4-5/76)	Fluctuating Load (6/1-6/14/76)	Net Change During Fluctuating Load Testing
Inlet SO_2, (ppm-avg.)	2,250	2,150	Decrease
SO_2 Removal, (% of Inlet-avg.)	96.5	97.5[a]	Increase
Inlet O_2, (vol. %-avg.)	6.5	7.5	Increase
Thickener Liquor Composition:			
Na^+_{acc}, (M)	0.35-0.4	0.33-0.38	No Change
$SO_4^=$, (M)	0.7-0.75	0.65-0.74	No Change
Cl^-, (M)	0.25-0.33	0.33-0.22	Decrease
System Oxidation, (% of SO_2-avg.)	17.5	~20[b]	Increase
Lime Utilization, (% of avail. lime-avg.)	93	91[c]	Increase[c]
Waste Solids, (wt. % solids-avg.)	54	52[d]	Decrease[d]

[a] During periods when SO_2 monitors operating and no mechanical problems.

[b] Estimated oxidation based upon a few data points.

[c] Slight decrease in the estimated lime utilization is not considered significant - see text.

[d] Decrease due in part to filter adjustments and non-optimal filter operation during filter tests.

the principal performance characteristics compared with the stable load operation during Period 3.

1. SO_2 Removal

In general, there was little significant effect of gas load on SO_2 removal efficiency during the fluctuating load testing. SO_2 levels rarely exceeded 100 ppm and typically were below 50 ppm. The trend, of course, was for lower outlet loadings (higher removal efficiencies) at the low flue gas rates due to the tendency to overfeed absorbent liquor slightly. Frequently, outlet SO_2 levels ran below 20 ppm at 30% gas load. Of greater significance was the ability to control SO_2 removal during transition periods when gas load was being adjusted. Transition periods typically lasted about five minutes and during these periods there was no difficulty in maintaining or adjusting outlet SO_2 levels as required. Throughout the period, SO_2 removal averaged better than 97%, which is slightly higher than that achieved during the stable load testing.

2. System Chemistry (Sulfite Oxidation)

The system chemistry was quite stable and liquor compositions were almost identical with those of the stable load period. There was no apparent trend in the concentration of any species other than chloride, which decreased from about 0.13M (~11,500 ppm) to 0.23M (~8,000 ppm) in the regenerated liquor. There was a slight drop in chloride levels measured in the coal; however, the decrease in chloride corresponding to the drop in liquor concentration was within the error band for the analytical method used for determination of coal chloride content.

The absence of any significant change in the liquor composition suggests that the rate of sulfite oxidation experienced during fluctuating load testing was roughly the same (as a percentage of SO_2 absorbed) as during the stable load testing. Attempts were made to measure oxidation rates in the scrubber system based upon species balances across the venturi and absorber. Taking into account slight variations in oxygen levels during the balance intervals, estimated oxidation rates are only a few percentage points higher (as a percent of SO_2 absorbed) than oxidation rates at 90% load.

3. Lime Utilization

The average of the analyses for six cake samples taken during the fluctuating load tests shows a slight decrease in utilization (91%) compared with the average utilization during the stable load testing (93%). While there was a tendency to overfeed lime slightly during low load periods, it would not be expected that short periods of such overfeeding would significantly change utilization. Since the 91% is within the variance in the utilization for the stable load testing and because the average lime analyses for the entire third period of operation were used in calculating utilization, the 2.0% difference in utilization between stable and fluctuating load is not considered significant.

4. Waste Solids Properties

Only intermittent operation of the filter was required to keep up with the rate of solids production. Usually, one or two intervals lasting from four to eight hours each were sufficient. To some extent, the rate and timing of cake withdrawal were dictated by filter test conditions.

The filter cake produced during the fluctuating load testing was much the same as that produced during the prior two months of stable load testing. There was a slight decrease in the average solids content of the cake; however, this is attributed to adjustments made in the filter and non-optimal operation during filter testing (which was conducted throughout the fluctuating load interval). Sodium losses in the cake were in the same range as those during stable load testing.

5. System Operability

Overall system operability was excellent. Few problems were encountered in the system operation either during changes in load (or inlet SO_2 concentration) or with operation at the extreme load levels (30% and 100%).

One minor problem that did occur in the operation of the thickener overflow hold tank was due to inadequate surge capacity. The capacity of the hold tank at Scholz was sized for only a 10-minute holdup at design flow (5 minutes of surge with a 50% normal level). On two occasions, when all system tank levels were high due to excessive rainfall, there was insufficient surge capacity in the hold tank to accommodate the rapid change from 100% to 30% gas load. This resulted in overflow of liquor from the hold tank for a few minutes until flow rates and tank level set points could be adjusted to compensate for the overflow.

Based upon this experience, a minimum 30-minute holdup should be provided in the thickener hold tank.

D. PROCESS PERFORMANCE -- PARTICULATE TESTING

The last three weeks of the test program were devoted to testing the effects of fly ash on the process chemistry and overall system performance. Particulate loadings in the inlet flue gas were increased by deactivating all or part of the electrostatic precipitator. As shown in Figure V-10, the precipitator consisted of six sections, each of which could be independently deactivated. Extensive flue gas sampling was performed by York Research Corporation during these tests. Sampling included total particulate loadings, chloride concentration and total sodium levels. Chloride sampling was conducted to determine chloride absorption efficiency, and sodium analyses were performed to confirm the entrainment data obtained by Guardian Testing Services during Period 8.

General operating conditions over the three-week period are listed in Table V-13. Principal control variables adjusted during the period

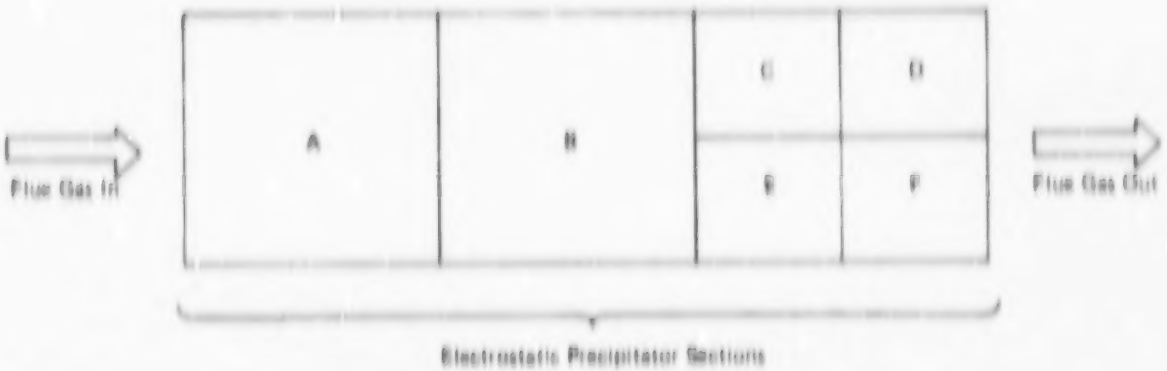


FIGURE V-10 SCHEMATIC OF THE ELECTROSTATIC PRECIPITATOR ON BOILER #1 AT SCHOLZ STEAM PLANT

TABLE 4-22

SUMMARY OF SYSTEM OPERATING CONDITIONS
PARTICULATE TESTING
(6/25-7/2/76)

	Range	Average
Inlet Flue Gas:		
Flue Gas Rate, (approx. lbs)	11-35	19
(% of design load)	55-170	85
SO_2 Level, (ppm)	1,500-2,700	2,100
O_2 Level, (vol. %)	5.5-8.5	7
Temperature, (°F)	290-340	~335
Fly Ash, (grains/scf dry)	0.82-3.6	—
Venturi Scrubber:		
Pressure Drop, (inches of water)	12-17	—
Liquor Recirculation Rate, (L/G-gals./Mscf)	—	~20
Spray Tower:		
Total Pressure Drop, (inches of water)	3.5-5	4.5
Liquor Recirculation Rate, (L/G-gals./Mscf)	—	7
Thickener Liquor Composition:		
pH	11.8-12.4	12.2
Active Sodium (ΣNa^+)	0.35-0.42	0.38
$SO_4^=$, (%)	0.65-0.90	0.80
Cl^-, (ppm)	4,000-4,500	4,700

were the number of precipitator sections in service, gas flow rate, and venturi pressure drop. Figure V-11 shows the precipitator operation and Table V-13 lists the conditions for the specific scrubber tests performed. All scrubber tests were conducted with the flue gas reheater off.

Particulate loadings measured in the inlet flue gas were found to be fairly insensitive to the number of precipitator sections deactivated, but rather were a function of whether or not the precipitator was in service. With sections A and B in operation, inlet loadings ranging from 0.017-0.025 grains per dry standard cubic foot (gr/scfd) were measured. With section A alone, loadings were only slightly higher, 0.018-0.084 gr/scfd. But with all sections deactivated, measured loadings ranged from 2.29-3.60 gr/scfd at the scrubber inlet.

Inlet SO_2 levels during the last three weeks decreased slightly from levels experienced in the previous fluctuating load testing. Levels ranged from as low as 1,500 ppm to as high as 2,700 ppm, and averaged about 2,100 ppm. Oxygen concentrations in the flue gas varied from 5.5% to 8.5% and typically ran about 7.0%.

Except for one brief interval during gas sampling for entrainment losses at low load, the flue gas rate was maintained at or above 85% of design load. The average flue gas rate ran about 95% of design load.

As in other operating periods, thickener liquor composition reflected the variations in inlet flue gas conditions. Soluble sulfate levels ranged from 0.65M to 0.90M, increasing at low inlet SO_2 levels and high oxygen concentrations (as system oxidation increased). Typically, sulfate concentrations ranged from 0.7M to 0.85M. Active sodium levels and chloride concentrations remained fairly constant throughout -- 0.35-0.42M Na^+ active and 0.22-0.26M Cl^-. This range of chloride levels was established with inlet chloride concentrations of approximately 30 ppm (1.5% of the average inlet SO_2).

Table V-14 summarizes the general system performance. Important performance characteristics are discussed in the following section.

1. Particulate Removal

The particulate removal capability of the scrubber system was tested with the venturi operating at a pressure drop of both 13 inches and 17 inches of water and at three inlet particulate loadings. The results of the particulate measurements for each test condition are given in Table V-15. Standard EPA sampling and analytical procedures were used in all tests.

As would be expected, outlet particulate loadings increased slightly with increasing inlet loadings, but there was no statistical difference between outlet particulate loadings (or particulate removal efficiencies) measured at venturi pressure drops of 13 inches and 17 inches of water.

TABLE V-13

SUMMARY OF SCRUBBER TEST CONDITIONS

Test No.	Gas Flow (% of design)	Precipitator Sections in Service	Venturi ΔP ("H O)	Flue Gas Sampling
1	100	A&B	12	Particulate
2	100	A&B	12	Particulate
3	100	A&B	12	Particulate
4	100	A&B	17	Particulate
5	100	A	17	Particulate
6	100	A	12	Particulate
7	100	A	12	Particulate
8	100	A-F	12	Sodium
9	100	A-F	12	Sodium
10	55	A-F	12	Sodium
11	55	A-F	12	Sodium
12	100	A-F	5	Chloride
13	100	A-F	5	Chloride
14	85	A-F	12	Sodium
15	85	A-F	12	Sodium
16	100	None	17	Particulate
17	100	None	17	Particulate
18	100	None	17	Particulate
19	100	None	12	Particulate
20	100	None	12	Particulate
21	100	None	12	Particulate

TABLE V-1A

SUMMARY OF SYSTEM PERFORMANCE

Inlet Flue Gas:	
SO_2, (ppm)	1,500-2,700
O_2, (ppm)	5.5-8.5
Cl^-, (ppm)	~30
Particulate, (grs/scfd)	0.017-1.60
Performance:	
SO_2 Removal, (avg. % of inlet)	~98
Outlet Particulate, (grs/scfd)	0.010-0.037
Cl^- Removal, (avg. % of inlet)	99+
Lime Utilization, (% of available $Ca(OH)_2$)	97
Filter Cake, (wt % solids-avg.)	56
(wt % acid insolubles)	6.2-41
(mole $CaSO_4$/mol $CaSO_3$)	0.09-0.11
Liquor Entrainment--102% load, (ppm)[a]	0.0052[a]
92% load, (ppm)[b]	0.013[b]
83% load, (ppm)[a]	0.0037[a]
57% load, (ppm)[a]	0.0030[a]

[a]Gas sampling by York Research Corporation (June 1976), average of two data points each

[b]Gas sampling by Guardian Systems (December 1975), average of five data points

TABLE V-13

SUMMARY OF PARTICULATE TEST RESULTS

General Conditions:

100% gas load
Reheater off
Venturi L/G = 20 gals./kacf sat'd

Precipitator Sections in Service	Inlet Loading (grs/scfd)	Test Nos.	Average Outlet Loading	
			ΔP = 12" H_2O	ΔP = 17" H_2O
A&B	0.017-0.025	1-3	0.010-0.015	--
A&B	0.018	4	--	0.011
A	0.034, 0.047	6,7	0.021, 0.027	--
A	0.084	5	--	0.026
None	2.95-3.60	19-21	0.024-0.037	--
None	2.29-3.34	16-18	--	0.033-0.037

Normally, it would be expected that the increased pressure drop would increase removal efficiency, particularly at the higher inlet loadings. That the outlet loadings were the same at both pressure drops can only be attributed to the presence of the absorber (with two trays) following the venturi. The average removal efficiency of the combined venturi and absorber for periods when the precipitator was out of service was 98.9%.

The quantity of fly ash added to the system ranged from 10-50 pounds per hour (0.5-2.5% of the dry cake weight) with the precipitator in service, to 1,000-1,600 pounds per hour (25-45% of the dry cake weight) with the precipitator out of service.

2. SO_2 Removal

Outlet SO_2 levels throughout the particulate testing period rarely exceeded 100 ppm and were consistently below 50 ppm. As a result, the average SO_2 removal efficiency during these last three weeks was better than 98%. On only half-a-dozen occasions, for periods up to a few hours, did the outlet SO_2 rise above 200 ppm. These occurred either because of temporary mechanical problems or because of calibration/certification testing of the SO_2 monitors when it was necessary to maintain outlet SO_2 levels on the order of 700 ppm.

3. Chloride Removal

In the two tests run during June (Tests 12 and 13, Table V-11), chloride levels of approximately 25 ppm were measured in the inlet flue gas. Corresponding outlet levels ran below 0.25 ppm -- a chloride removal efficiency of 99%. This level of chloride absorption is consistent with the equilibrium level of chloride established in the system liquor, as dictated by chloride absorption and losses of chloride in the waste cake. The measured inlet chloride concentration, however, is about half that expected based upon chloride and sulfur analyses of the coal. The measured chloride levels in the gas correspond to about 1% of the inlet SO_2 level (25 ppm Cl^- and 2,100 ppm SO_2). Coal analyses show about 0.1 wt % Cl^- and 3.5 wt % sulfur on the average, or a chloride content of about 2.5% of the sulfur value on a mol basis. Since very little chloride was found in the ash, this discrepancy must be attributed to analytical error in the coal analyses due to the low accuracy in the analytical procedures.

4. Lime Utilization

Lime utilization during particulate testing averaged approximately 97% of the available $Ca(OH)_2$ in the raw lime feed based upon cake analyses and average analyses of the raw lime throughout Period 3. Based upon lime sample analyses for the last three weeks only, the utilization was 95%. As in the case of fluctuating load testing, the particulate testing period was too short to calculate accurate overall system material balances that would confirm these utilization figures. However, based upon the fact that all but one of the cake analyses showed a utilization higher than the average utilization for the stable load period (April-May,

(1/h), it is probable that there was a slight improvement in utilization during particulate testing. This can be attributed to the slightly lower operating pH's (extent of regeneration) and slightly lower inlet SO_2 levels which allowed slightly more holdup time in the reactor.

3. System Chemistry (Oxidation and Sulfate Control)

There was very little change in the system chemistry throughout the particulate load testing, and very little real difference between solution compositions during particulate testing and stable load testing. The system operated slightly more concentrated in total sodium during particulate testing. The sulfate level in the system increased on the average by about 10-15%; however, the active sodium concentration increased also. The active sodium-to-sulfate ratio was, at most, 10% higher during particulate testing than during stable load testing.

Since oxygen levels in the flue gas were relatively the same during both stable load and particulate testing, the absence of any significant change in the system chemistry suggests no major effect of fly ash on oxidation. This was confirmed by the few data points that could be obtained on scrubber system oxidation (by scrubber system material balances). The absolute oxidation (lb mole/min) agreed quite closely with those obtained during stable load testing.

There was a slight increase, though, in oxidation relative to SO_2 removal due to the lower inlet SO_2 levels during particulate testing. On the average inlet SO_2 levels (and amount of SO_2 removed) decreased about 10% from stable load to particulate testing. Therefore, about a 10% increase in oxidation would be expected relative to SO_2 removal. This is confirmed from $CaSO_4/CaSO_3$ ratios in the cake. The average $CaSO_4/CaSO_3$ ratio (mol basis) in the cake for particulate testing was 0.11 (0.09-0.13) compared with about 0.10 for stable load testing.

4. Waste Cake Properties

The solids content of the waste cake increased slightly during particulate testing. The average cake solids content for stable load testing was 54%, while for particulate testing it was 56%. Some of the cake withdrawn during particulate testing had very little fly ash and some was filtered at unusually low filter vacuum -- 8 inches to 12 inches during the particulate testing period versus 11 inches to 16 inches during stable load testing. Discounting the periods of low vacuum, the average solids content of cake containing greater than 20% ash was about 4-7% higher than comparable cake without ash.

The washability of the cake with fly ash was comparable to or possibly slightly better than that without ash; however, there is insufficient data to provide a clear-cut correlation. The soluble sodium losses in the cake at roughly equivalent wash ratios (and filter vacuum) were slightly less when the cake contained significant fly ash.

Even though the cake had a higher solids content and appeared to wash more easily, it did feel somewhat wetter. This apparent wetness may have been due to the added lubricity from the spherical fly ash particles.

It is interesting to note that when dumped and left at the disposal pond, the cake containing fly ash tended to agglomerate into chunks and harden somewhat, while cake without ash did not. This hardening was also noticed in the solids that remained in the thickener about a month after the system was shut down following completion of the test program.

7. Liquor Entrainment

Measurements of entrained liquor in the scrubbed gas leaving the absorber were made in December 1975 by Guardian Testing Services and in June 1976 by the York Research Corporation using sodium as a tracer. The York data are summarized in Figure V-13. The highest levels of entrainment measured (@ 92% gas load by Guardian) averaged approximately 0.013 gpm. This corresponds to about 0.022 grains of liquor per standard cubic foot of dry gas (=0.0025 grains of solids/scfd), which is equivalent to a sodium makeup requirement (as Na_2CO_3) of less than 0.1% of the SO_2 removal (mol basis). In subsequent sampling performed by York, entrainment was measured to be only about one-third this level (=0.008 grains of liquor/scfd). The sodium losses by entrainment, therefore, are so small that they can be considered negligible.

In the sampling performed in June it was also found that the grain loading of liquor (or sodium salts) was almost constant over the range of gas rates tested. Therefore, the volume of liquor lost decreased almost linearly with gas flow. This suggests that the mist eliminator was operating optimally at design gas flow -- removing all but a fine mist that also was carried through at lower gas flows.

8. Overall Operability

There were no deleterious effects of the fly ash either on the process or mechanical operability or reliability. In fact, the fly ash had some beneficial effects (e.g., improved cake properties). However, particulate testing was of too short a duration to test long-term effects of the fly ash on materials of construction.

E. MECHANICAL PERFORMANCE

The equipment performance in terms of overall reliability is reflected in the system availability, the level of maintenance required, and the overall operability (ease of operation) of the system. In general, the equipment performance was quite good, although there were equipment and instrumentation problems. Most of these problems were mechanical in nature and resulted from design or fabrication oversights commonly associated with a first-of-a-kind prototype system. There were only a few problems encountered that reflected process chemistry, and these required simple operational and/or equipment adjustments.

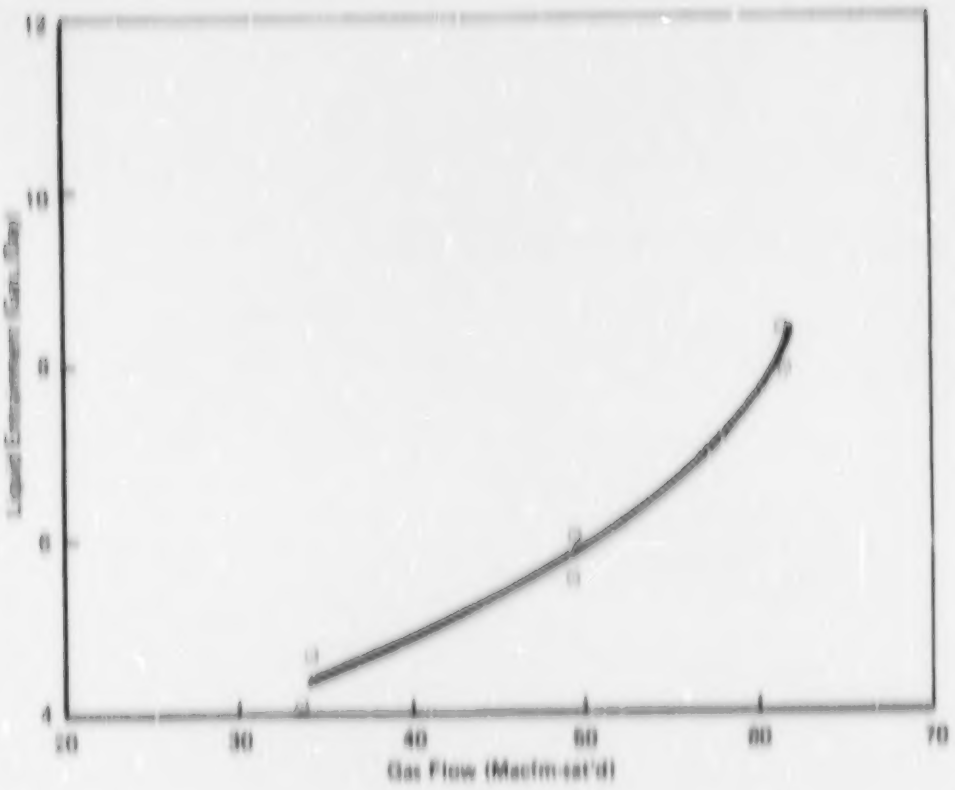


FIGURE V-12 LIQUOR ENTRAINMENT VS GAS FLOW MEASURED BY YORK RESEARCH (6/76)

Appendix G contains a detailed list of equipment and instrumentation problems encountered during the program. Included in the list are a number of problems of the type that would normally be expected to occur during startup or items normally associated with routine maintenance. The fact that some of the problems shown were not immediately corrected is an indication that they were either of minor significance or did not cause important operational difficulties. The more important problems are discussed in the following sections.

1. Equipment

The mechanical equipment problems and maintenance items of primary concern are reviewed by process subsection. The order in which each subsection is discussed generally reflects the frequency or number of problems encountered or degree of maintenance required.

a. Filter

The filter was the largest source of problems in the prototype system. Because of anticipated corrosion problems associated with high chloride levels, a large part of the filtration equipment was fabricated out of fiberglass, which is not as sturdy as stainless steel and more prone to failures at stress points in the construction. Filter problems during Period 1 included:

- erosion of the fiberglass scraper blade, resulting in jagged edges which tore the cloth
- erosion of the bridge valve due to solids carried through cloth holes
- loss of vacuum due to cracks in the internal drum trunnion tubes
- cracking of the plastic caulking strips, allowing retention ropes to loosen and releasing the cloth panels
- failure of the fiberglass rocker arm used to agitate the slurry in the filter tub

Modifications were made to the filter during the latter part of Period 1 and the early part of Period 2. These modifications included replacement of the fiberglass scraper blade with one fabricated out of stainless steel, reinforcement of the rocker arm with stainless steel plates, and the design of a new method for retaining the filter cloth panels. These changes along with regular inspection and maintenance and increased familiarity of Gulf Power personnel with the equipment significantly improved filter performance.

During the scheduled boiler shutdown for annual maintenance in January and February 1976, the filter drum was overhauled by the manufacturer

and permanent cloth retention strips of the new design were installed. Following this overhaul (Period 3) there were fewer problems with the filter operation.

b. Reactor System

Two equipment problems of note were encountered in the reactor system: plugging of the dry lime feed chute when dry lime was fed directly to the first reactor, and buildup of solids in the first reactor. The chute plugging problem was caused by hot vapors rising from the first reactor into the chute entrance port, condensing and wetting the lime. The problem was resolved by installation of a vibrator on the feed chute with provision for injection of air near the flange connection to prevent vapors from rising into the chute. Of course, no chute plugging occurred when lime was fed as a slurry as it would be fed in a full-scale application.

Solids buildup in the first reactor was a function of the manner of lime feed (dry versus slurry lime), dry lime feed chute location, the degree of agitation, and operation of the reactor under upset conditions (e.g., gross overfeeding of lime). Deposition of solids occurred both above and below the liquid surface, particularly in the area near the feed chute. While the problem was never serious enough to cause shutdown of the system, it did require occasional cleaning. The rate of buildup averaged about 0.75-1.0 inch per month.

A simulation of the conditions in this reactor at the CEA/ADL pilot plant in Cambridge was successful in confirming the source of the solids buildup and a new first reactor was installed prior to the start of the third operating period. The lime slurry feed system was also activated as an alternative to the feeding of dry lime. (Feeding a slurry of slaked lime would be the normal practice in a full-scale application because of the high cost of direct purchase of dry hydrated lime.) The new reactor and use of slurried lime minimized, but did not eliminate, the buildup. Agitation was still poor and process upsets continued. However, with improved agitation and process control, it is expected that such buildup would, at worst, be a semi-annual maintenance item. Such maintenance would not require system shutdown since flow can be switched to a parallel reactor train, or the first reactor can simply be bypassed.

An additional problem was the abrasive wear of the flake lining on the floor of the second reactor in the area directly beneath the agitator. This lining was replaced with Neil Rigifloor 4130 prior to Period 3. The Rigifloor showed no evidence of wear after three and one-half months of service in Period 3.

c. Scrubber

The principal equipment problems in the scrubber system involved control and block valves, and vessel linings.

Valves

Erosion and debonding of rubber linings in the bleed control valves and recycle block valves on both the absorber and venturi occurred during Periods 1 and 2. These failures were due to the high degree of throttling required to control flow. The valves were sized to accommodate the much higher flows associated with direct slurry scrubbing. The rubber-lined control valves were replaced with 316 stainless steel valves prior to Period 3, and the block valves replaced either with spool pieces or new rubber-lined valves. Inspection of the control valves following completion of the test program in July 1976 (three and one-half months of service) showed them to be free of corrosion, erosion, or scale.

Vessel Linings

Lining problems occurred in both the venturi and absorber. For the most part, these were corrected by patching or replacement of the lining with a different material.

In the absorber a few pinholes and hairline cracks occurred in the Heil 4850 Flakeline on the vessel walls, particularly near pressure and temperature tap holes. These appeared during the first period of operation (in the first five months). The holes were patched prior to resuming operation in Period 2 and no similar failures occurred. However, after system shutdown at the completion of the test program, discrete points of lining wear were found on the sharp edges of the duct expansion joint connection between the venturi and absorber. As expected, the carbon steel at these points was corroded.

In the venturi there was erosion of the original Heil 4850 Flakeline on the liquor distribution shelf under the tangential nozzle discharge. The shelf was relined with Rigiflour 4130 (the same material used on the floor of Reactor 2) prior to Period 3. After three and one-half months of service (March-July 1976) the Rigiflour was in excellent condition.

The lining on the venturi gas inlet in the quench zone deteriorated. The area was relined with Plastite 4030 prior to starting Period 3. After three and one-half months of service the Plastite lining on the outside of the downcomer showed no signs of failure; however, on the inside where it was in direct contact with hot gas, the lining was deteriorating. The reason for the failure is unclear (whether it was poor application, high temperature, or both), but the failure suggests that a corrosion resistant metal alloy may be most suitable for such areas.

Corrosion

In addition, there was evidence of stress corrosion cracking and pitting of stainless steel in the absorber internals. Most of this occurred on 304 stainless steel which was inadvertently substituted for 316/316L. (316/316L stainless steel was specified throughout). However, some

pitting occurred with 316. This 316 was found to be low in molybdenum content. Also in some welded applications, 316 was inadvertently substituted for 316L.

A slight corrosion and ash buildup on the fan during extended shutdowns was diagnosed to be due to flue gas leaks through the isolation damper. Since the fan was located upstream of the system and was constructed out of carbon steel, significant corrosion was not expected. The corrosion and ash buildup were minor and the fan rotor was easily cleaned and rebalanced when it occurred. Correcting the leak through the isolation damper by installing a new damper or use of an air seal system was considered to be unwarranted.

Pump Seals

Leakage of solution through the venturi and absorber pump seals was of concern primarily because it represented a loss of sodium from the system. Tests were conducted by Southern Company Services and Gulf Power personnel to determine the size of the leaks under various pump packing conditions and to determine how best to eliminate or minimize the leaks. A Teflon impregnated packing was installed just prior to the end of operating Period 3 and minimized packing failures and improved maintenance.

d. Thickener

The major problems with the operation of the thickener were plugging of the underflow lines (Period 1) and leaking of liquor through the bottom due to lining failure (Period 2). Plugging of the thickener underflow lines was partly due to the design of the underflow piping, and partly due to the frequent downtime on the filter which allowed thickener underflow slurry concentrations to exceed 30% solids. Redesign of portions of the underflow lines using flexible piping and adjustments to the operational procedures to maintain the underflow slurry concentration in the 15% to 25% range (by backflushing with clear hold tank liquor to dilute the underflow when necessary) effectively eliminated underflow plugging problems.

The leak that developed in the bottom of the thickener during the early part of the second period of operation was small but grew worse throughout Period 2. After shutdown in January all the solids were removed from the thickener and the liquor drained. Inspection of the inside of the thickener showed sections of flake lining to be failing due to poor curing or poor application by the lining supplier. The leaks were located and patched, and the sections of failed lining on the thickener walls replaced with Neil 4850. Holes were also drilled in the bottom of the thickener, and steel bolts were welded in to support the bottom and prevent flexing. These areas were patched with Rigiflour 4130. These measures essentially eliminated any further leaking during Period 3, and inspection of the lining following completion of testing showed the lining to be in good condition.

When the thickener was drained, pieces of rope and a flattened paint can were found in the area of the cone. These items undoubtedly contributed to difficulties with the thickener underflow system. A piece of rope had previously been extracted from a seized underflow pump during operation in Period 2.

During Period 3 no significant problems were encountered with the thickener or thickener filter interface.

f. Instrumentation

Instrumentation problems primarily involved the pH units, level transmitters, and soda ash feed solution control system. Other instrumentation problems occurred, but for the most part, these were minor.

a. pH Probes

The piping for the flow-through pH units originally installed throughout the system had a tendency to plug and the electrodes tended to coat with a fine film, causing a drift in pH readings. In the case of the pH unit in the reactor system, the lines and probe chamber plugged completely with solids at low slurry flow rates and the probes eroded and broke at high flow rates. The flow-through unit on the reactor system was replaced with an immersion unit fitted with a sonic cleaner midway through Period 1. This proved to be much more reliable; however, there were problems keeping the sonic cleaner mounted on the probe casting. The unit required routine checking and recalibration about every week to two weeks. A Unilec immersion pH unit (Model No. 321) was installed without a sonic cleaner for testing during Period 3. This unit proved to be more reliable and accurate than the Leeds and Northrup unit with the sonic cleaner.

The take-off lines for the flow-through units on the scrubber system were relocated, and higher flow rates were maintained through the probes to prevent plugging of the piping. Since close pH control is not required, the problems with the pH units were not critical. The scrubber system can be operated on either the venturi bleed pH or outlet SO_2 (or, for that matter, inlet SO_2 and feed forward flow) with only occasional checks of the bleed pH to verify the SO_2 monitor. In fact, during a few weeks in the early part of Period 1, when all pH units and SO_2 monitors were out of service (due to delays in obtaining replacement parts), the system was successfully operated by taking hourly pH readings with a portable pH unit.

b. Level Transmitters

The original level transmitters installed in the system were generally unreliable. The particular type of unit used could not be completely serviced in the field. Thus, there were periods when inaccurate level indication and/or control caused operational problems. Starting in Period 2, these units were replaced as they failed with Foxboro transmitters. The Foxboro units performed acceptably.

c. Soda Ash Feed Control

The soda ash solution feed control system was also unreliable. This, in combination with occasional plugging of the feed gate on the dry soda ash feeder, made it difficult to close the overall material balance on sodium for short periods. During the last half of the second operating period, the sodium makeup rate was determined using frequent checks on the specific gravity of the soda ash solution and recalibration of the flow indicator along with the inventory of the soda ash silo and the quantity of soda ash delivery. Inventory and delivery information alone were not sufficient over the short term due to the large storage capacity in the silo and the low soda ash feed rates. Inventory and deliveries were used, though, for longer-term material balances during Period 1.

VI. REFERENCES

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4. Johnstone, H.F.; H.J. Read; and H.C. Blankmeyer, Recovery of Sulfur Dioxide from Waste Gases: Equilibrium Vapor Pressures Over Sulfite-Bisulfite Solutions, Industrial and Eng. Chem., 30 (1): 101-9, 1938.

VII. GLOSSARY

Active Sodium - Sodium associated with anions involved in SO_2 absorption reactions and includes sulfite, bisulfite, hydroxide and carbonate/bicarbonate. Total active sodium concentration is calculated as follows:

$$[Na^+]_{active} = 2 \times ([Na_2SO_3] + [Na_2CO_3]) + [NaHSO_3] + [NaOH] + [NaHCO_3]$$

Active Sodium Capacity - The equivalent amount of SO_2 which can be theoretically absorbed by the active sodium, with conversion to $NaHSO_3$. Active sodium capacity is defined by:

$$[Na^+]_{active\ capacity} = [Na_2SO_3] + 2 \times [Na_2CO_3] + [NaOH] + [NaHCO_3]$$

Calcium Utilization - The percentage of the calcium in the lime or limestone which is present in the solid product as a calcium-sulfur salt. Calcium utilization is defined as:

$$\text{Calcium Utilization} = \frac{\text{mols } (CaSO_3 + CaSO_4) \text{ generated}}{\text{mol Ca fed}} \times 100\%$$

Concentrated Dual Alkali Modes - Modes of operation of the dual alkali process in which regeneration reactions produce solids containing $CaSO_3 \cdot \frac{1}{2}H_2O$ or a mixed crystal containing calcium sulfite and calcium sulfate hemihydrates, but not containing gypsum. Active sodium concentrations are usually higher than 0.15M Na^+ in concentrated mode solutions.

CSTR--Continuous Stirred Tank Reactor - A well-agitated, baffled reactor vessel having a uniform concentration of species throughout. At any time the concentrations in the effluent from a CSTR are equivalent to those within the vessel.

Dilute Dual Alkali Modes - Modes of operation of the dual alkali process in which regeneration reactions produce solids containing gypsum ($CaSO_4 \cdot 2H_2O$). Active sodium concentrations are usually lower than 0.15M Na^+ in dilute mode solutions.

Sulfate Formation = The oxidation of sulfite. The level of sulfate formation relative to SO_2 absorption is given by:

$$\text{Sulfate Formation} = \frac{\text{mole } SO_4^{=} \text{ oxidized}}{\text{mol } SO_2 \text{ removed}} \times 100\%$$

Sulfate Precipitation = The formation of $CaSO_4 \cdot 2H_2O$ in soluble solids. The level of sulfate precipitation in the overall scheme is given by the ratio of calcium sulfate to the total calcium-sulfur salts produced:

$$\text{Sulfate Precipitation} = \frac{\text{mole } CaSO_4}{\text{mol } CaSO_x}$$

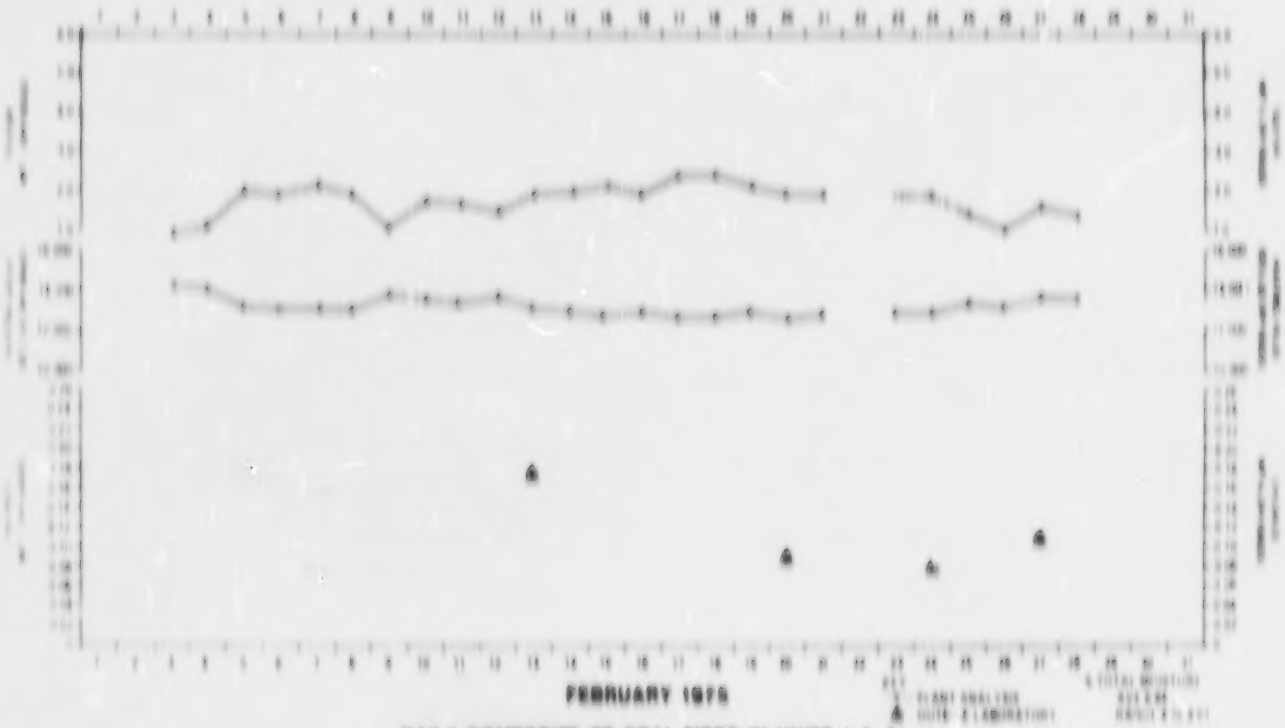
TDS--Total Dissolved Solids = Equivalent to the sum of all soluble species.

TOS--Total Oxidizable Sulfur = Equivalent to the sum of all sulfite and bisulfite species.

APPENDIX A

DAILY COAL ANALYSES

DAILY COMPOSITE OF COAL FIRED IN UNITS 1 & 2



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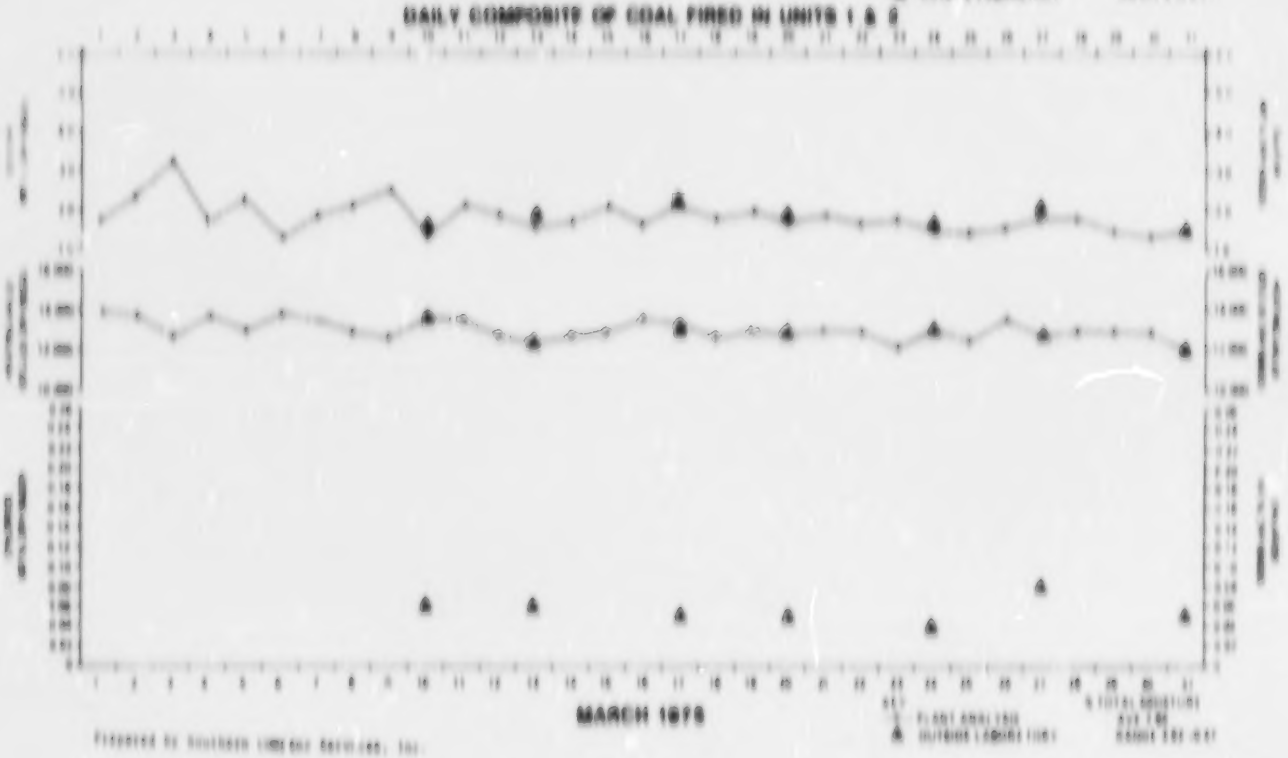

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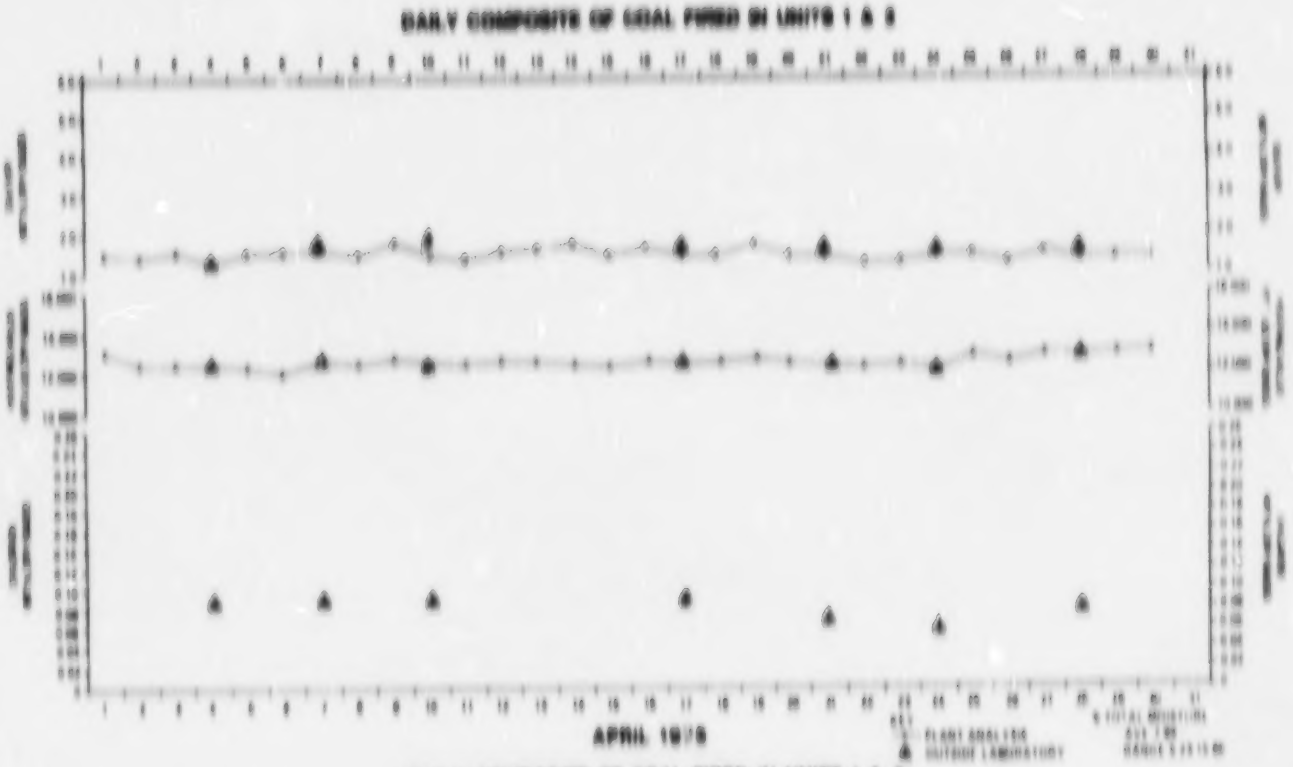
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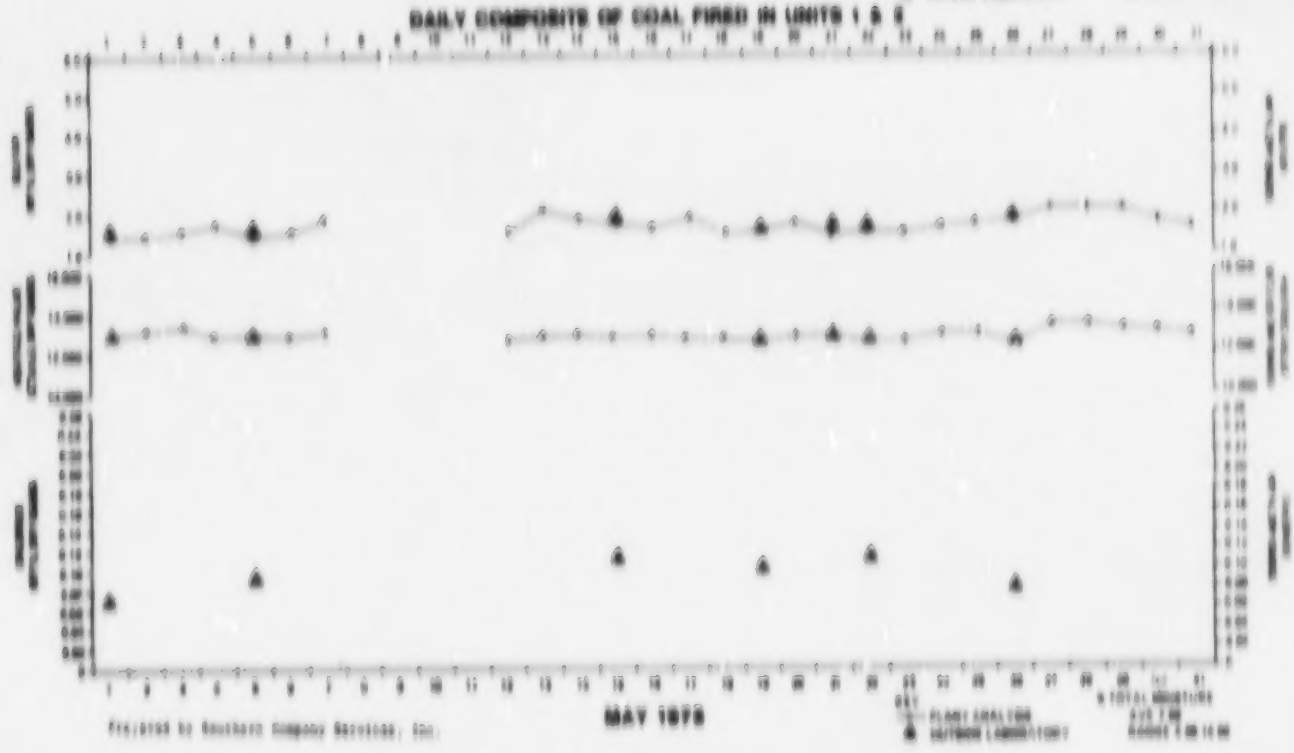
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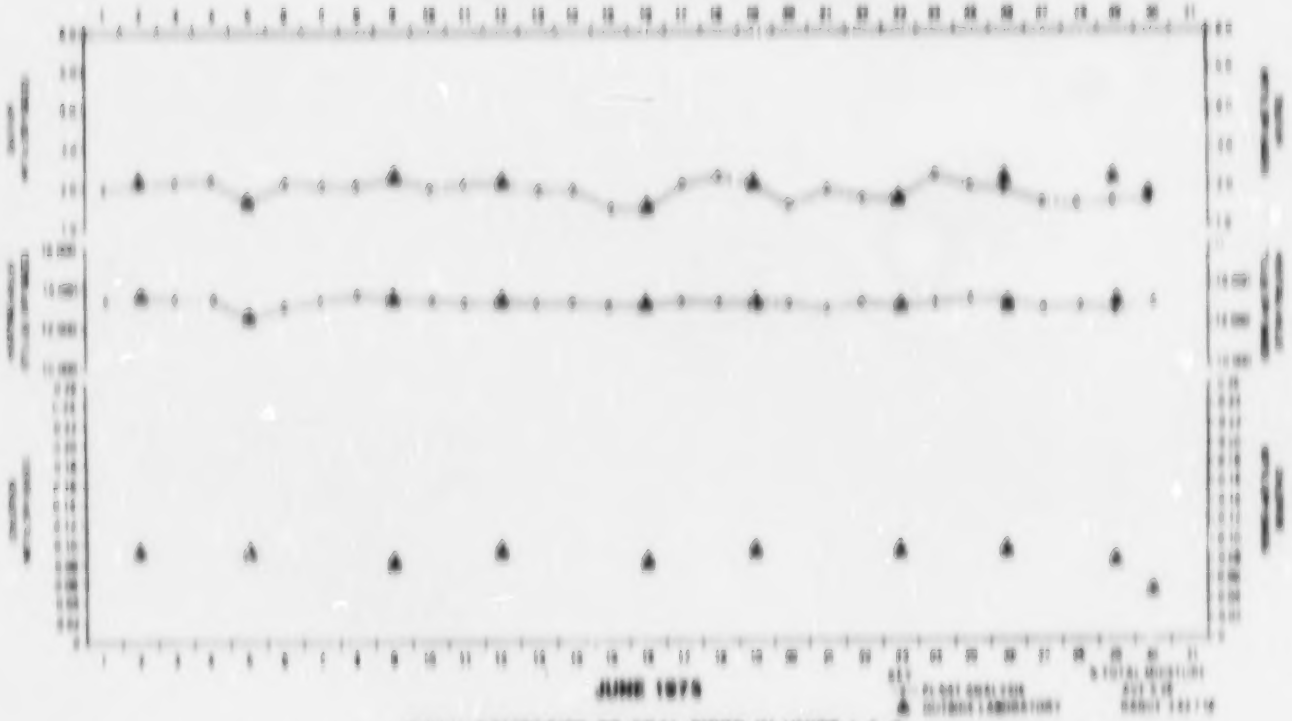

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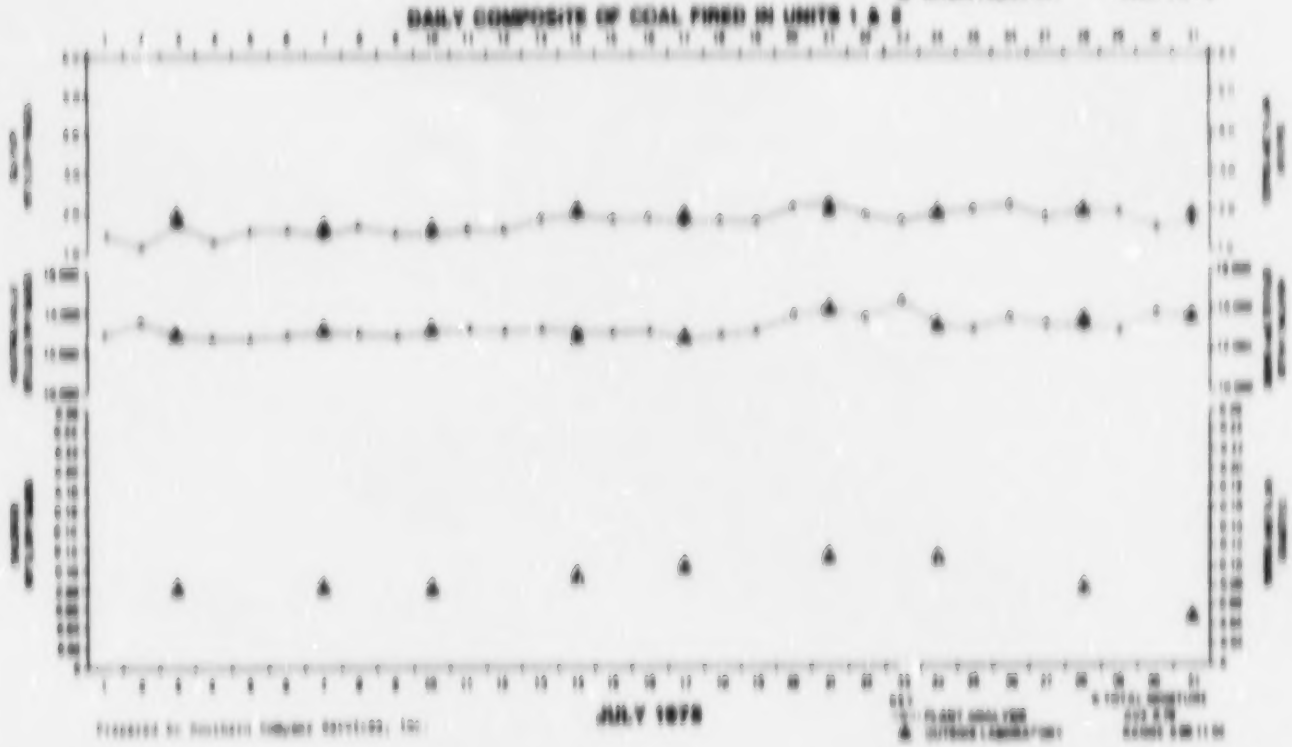

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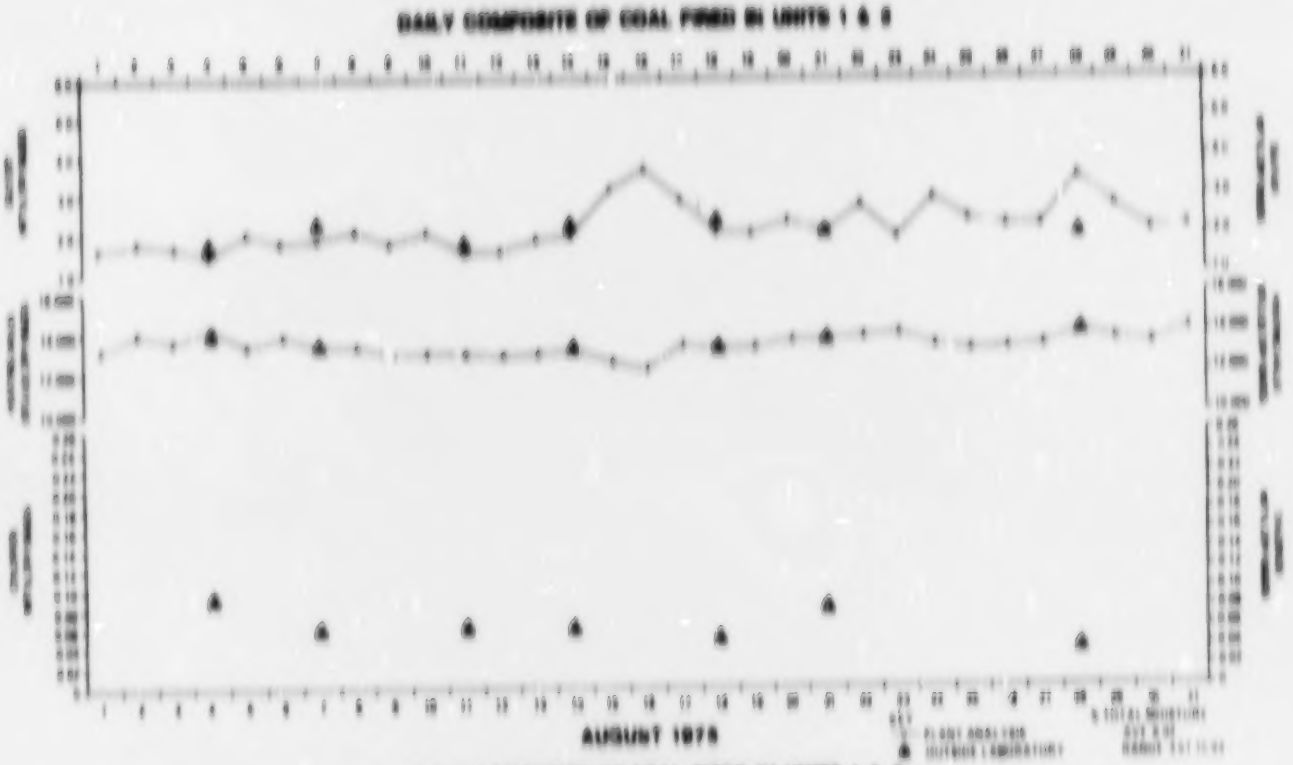

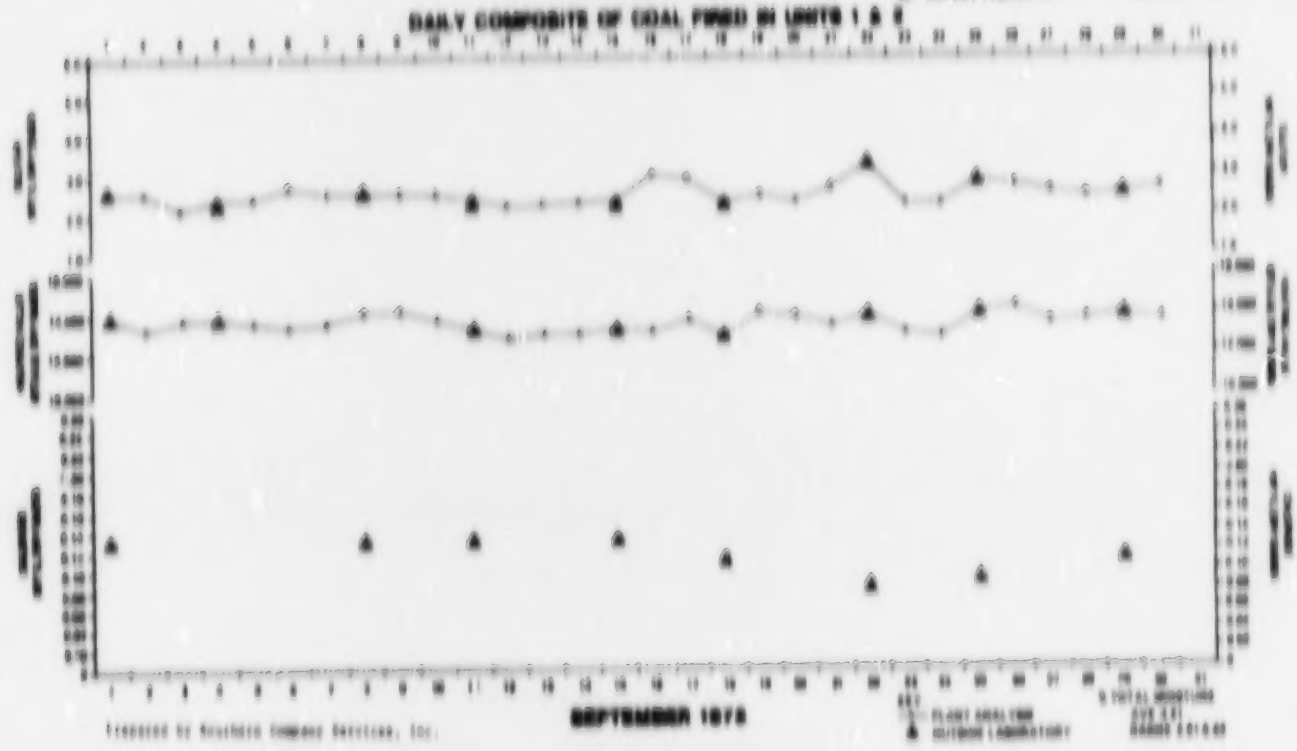

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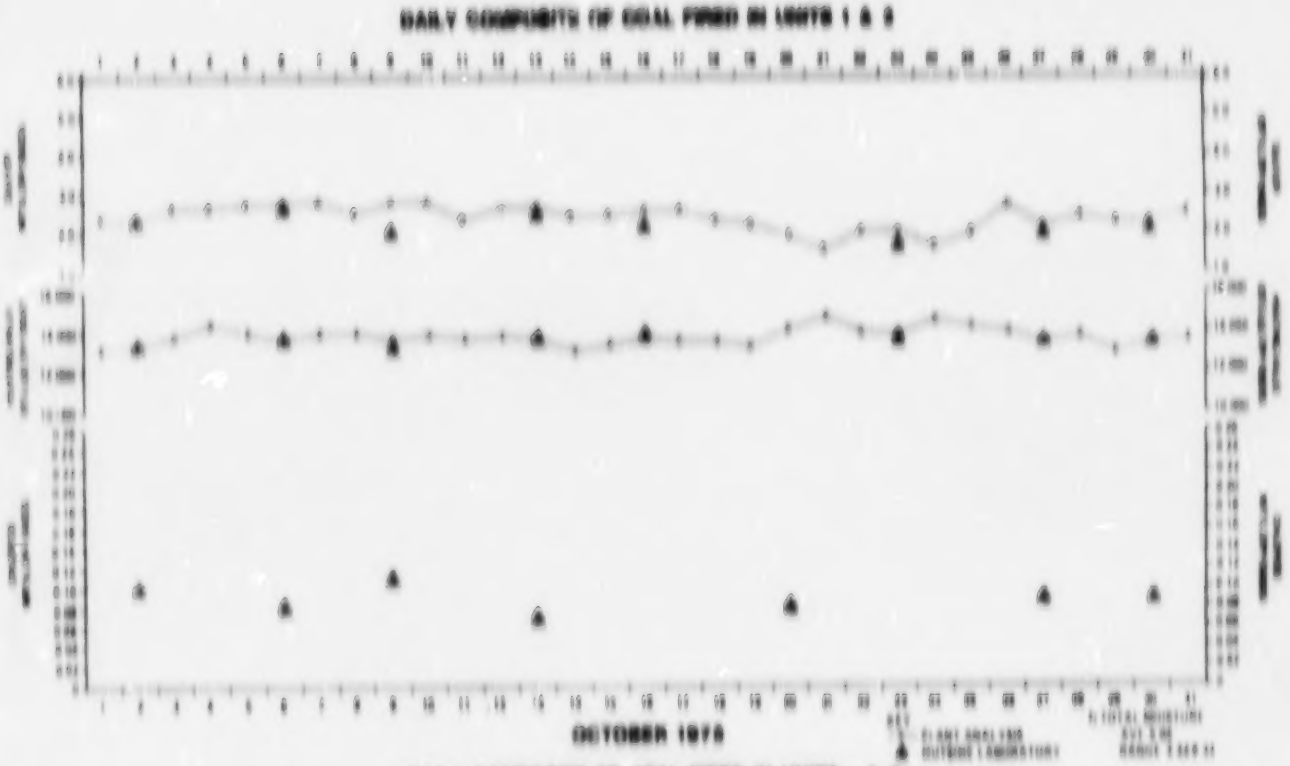

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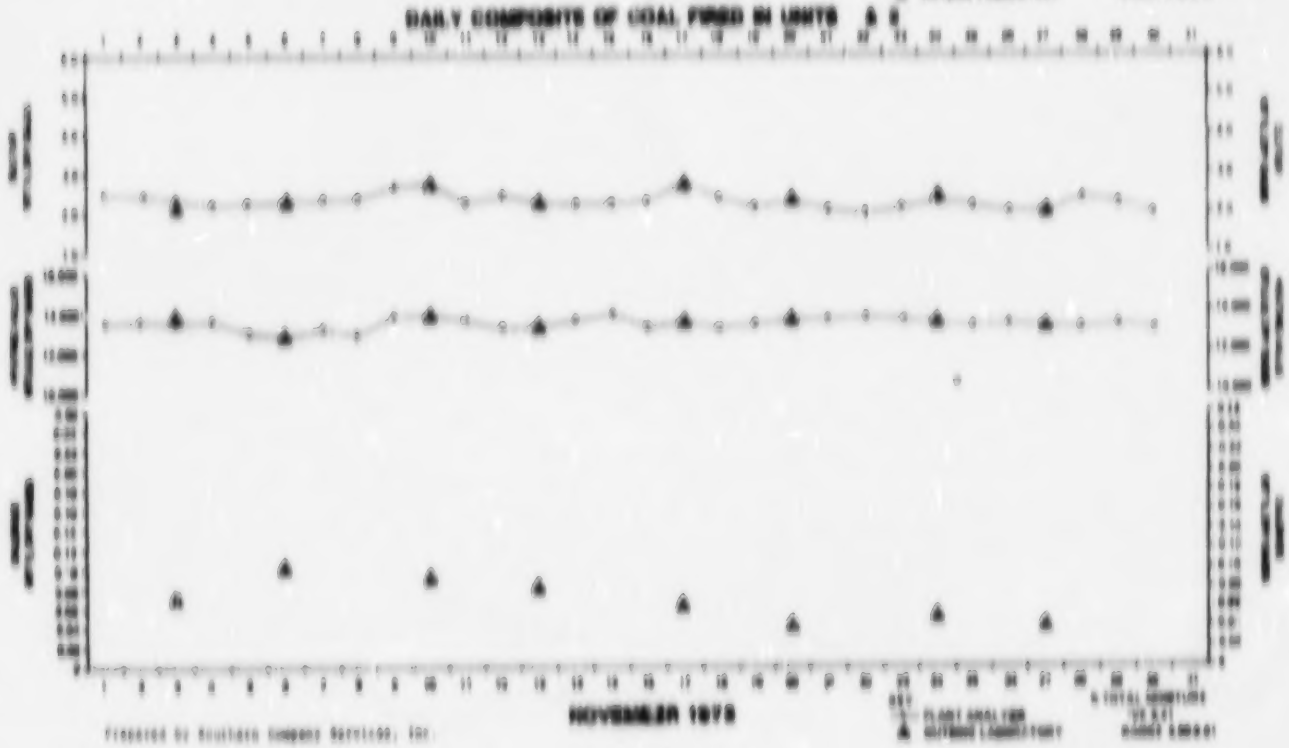

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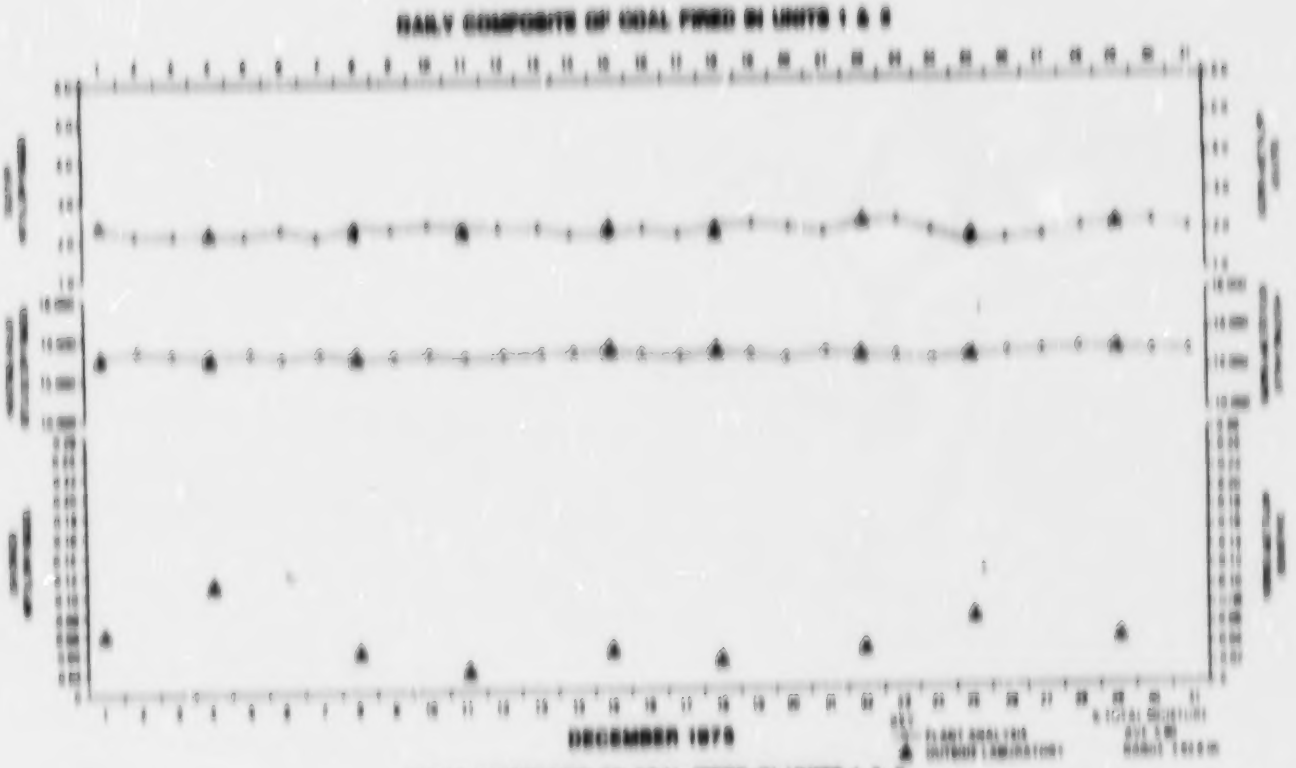

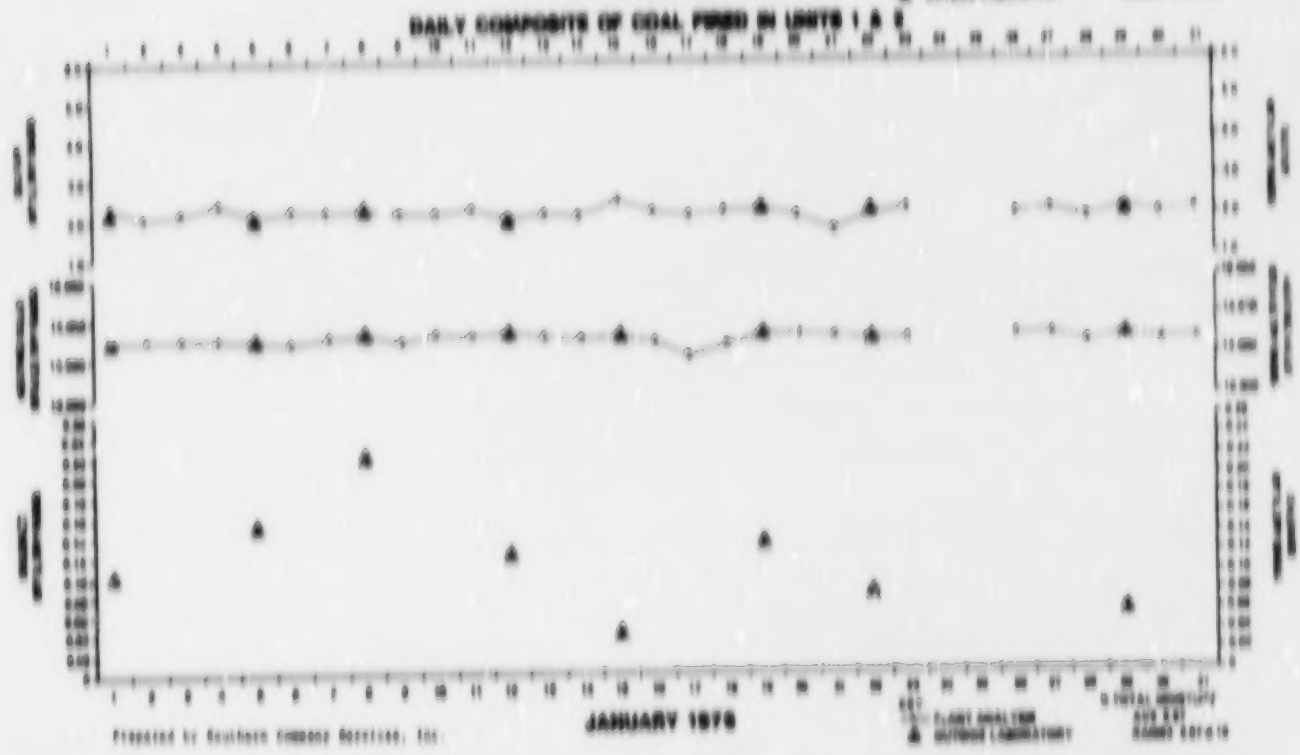

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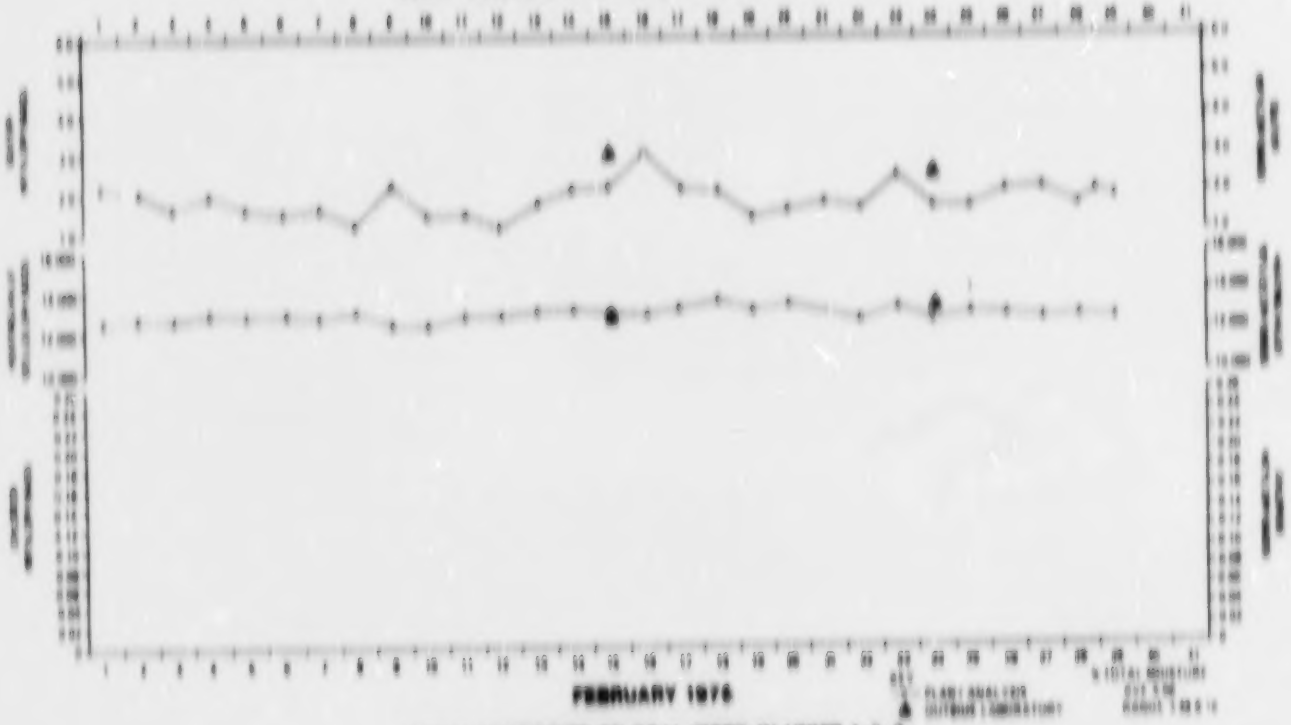
DAILY COMPOSITE OF COAL FIRED IN UNITS 1 & 2



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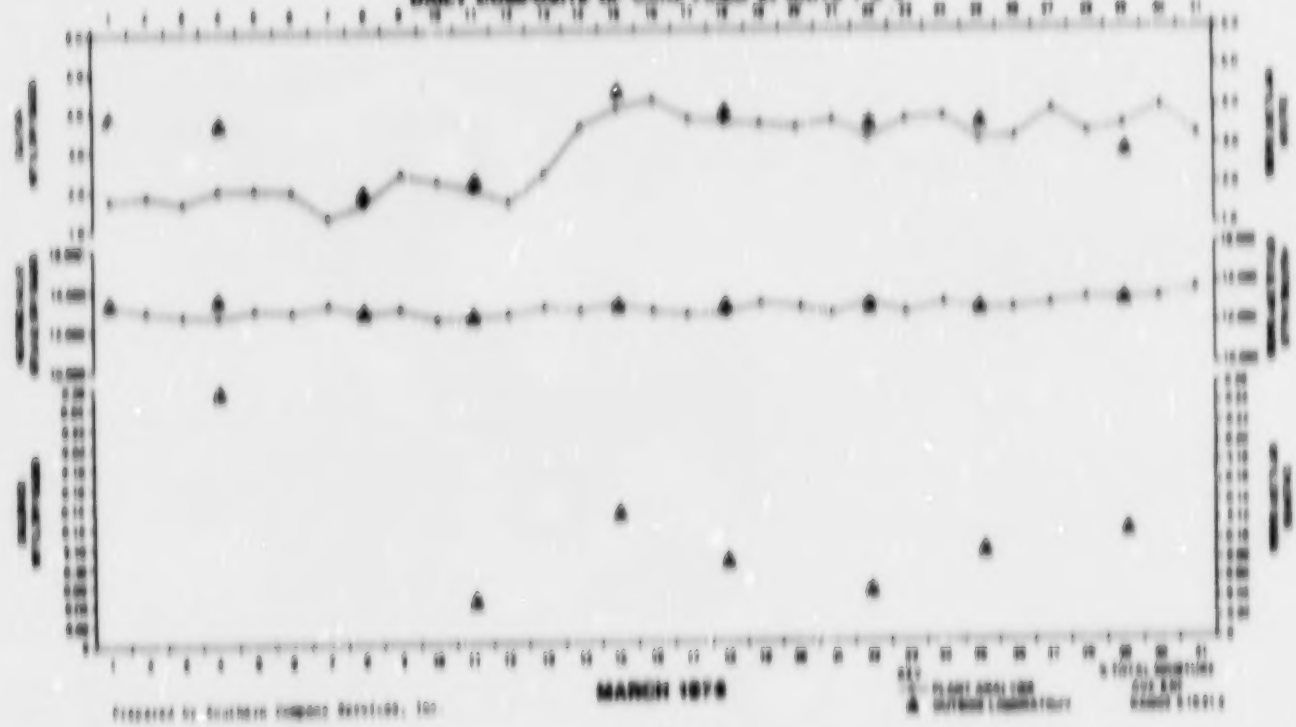

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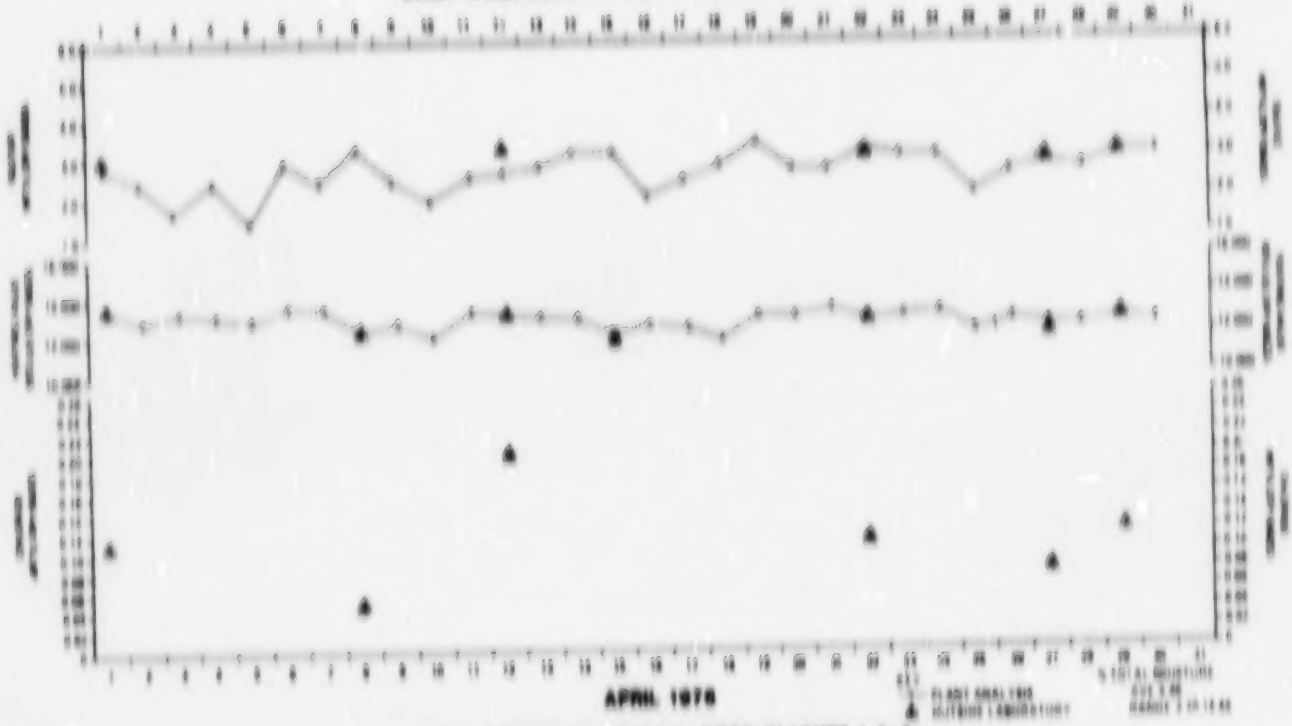

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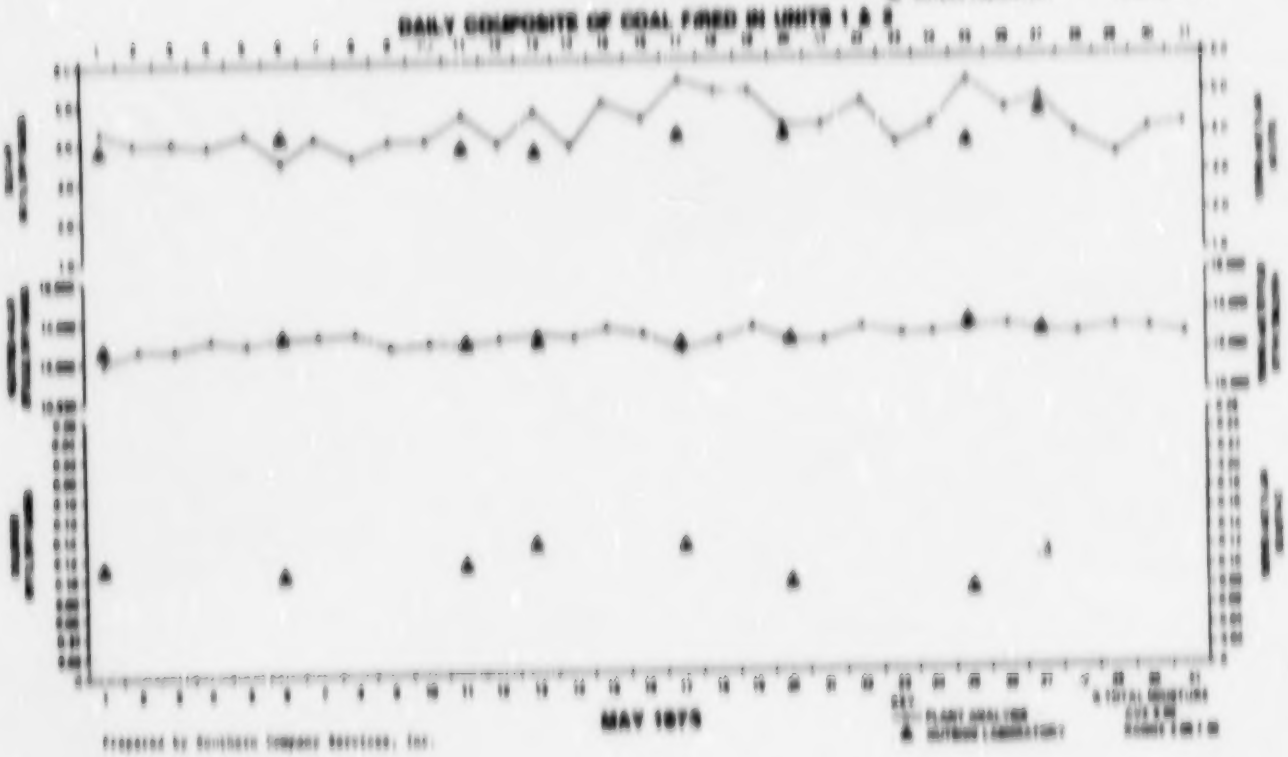

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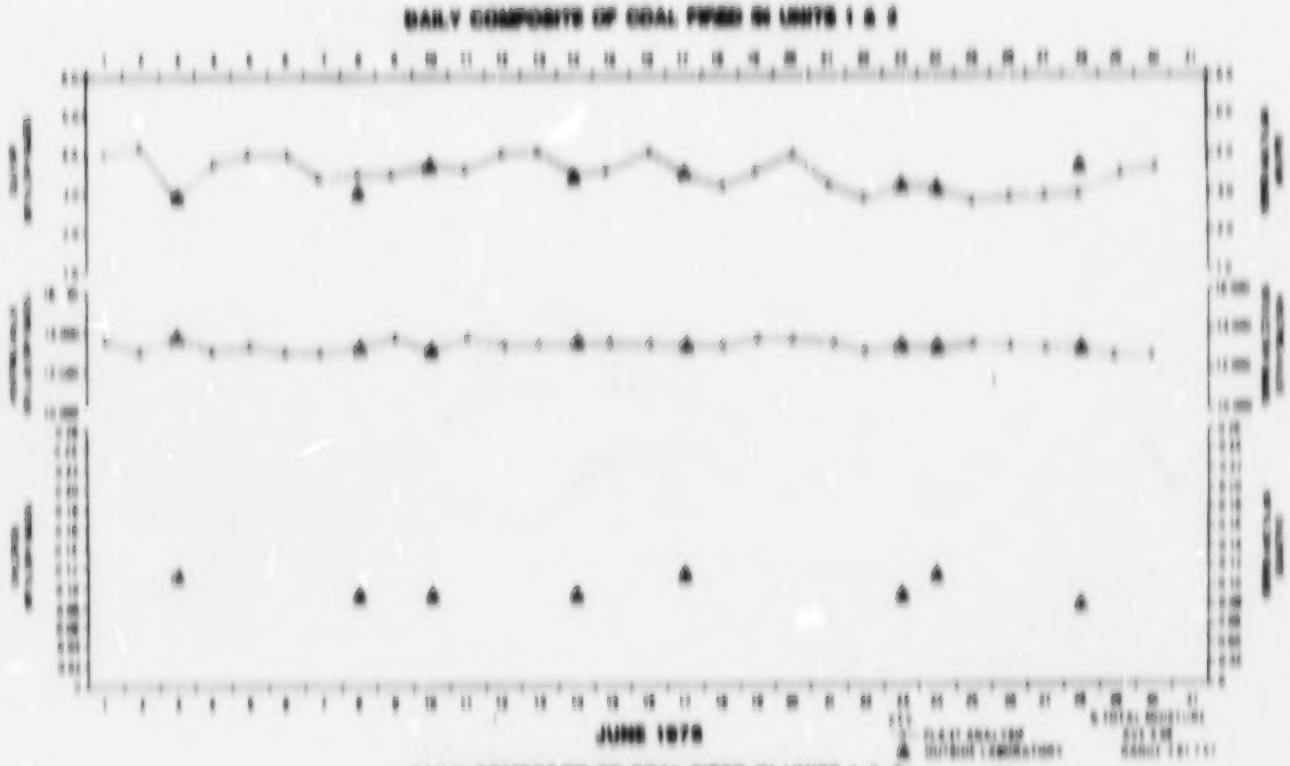
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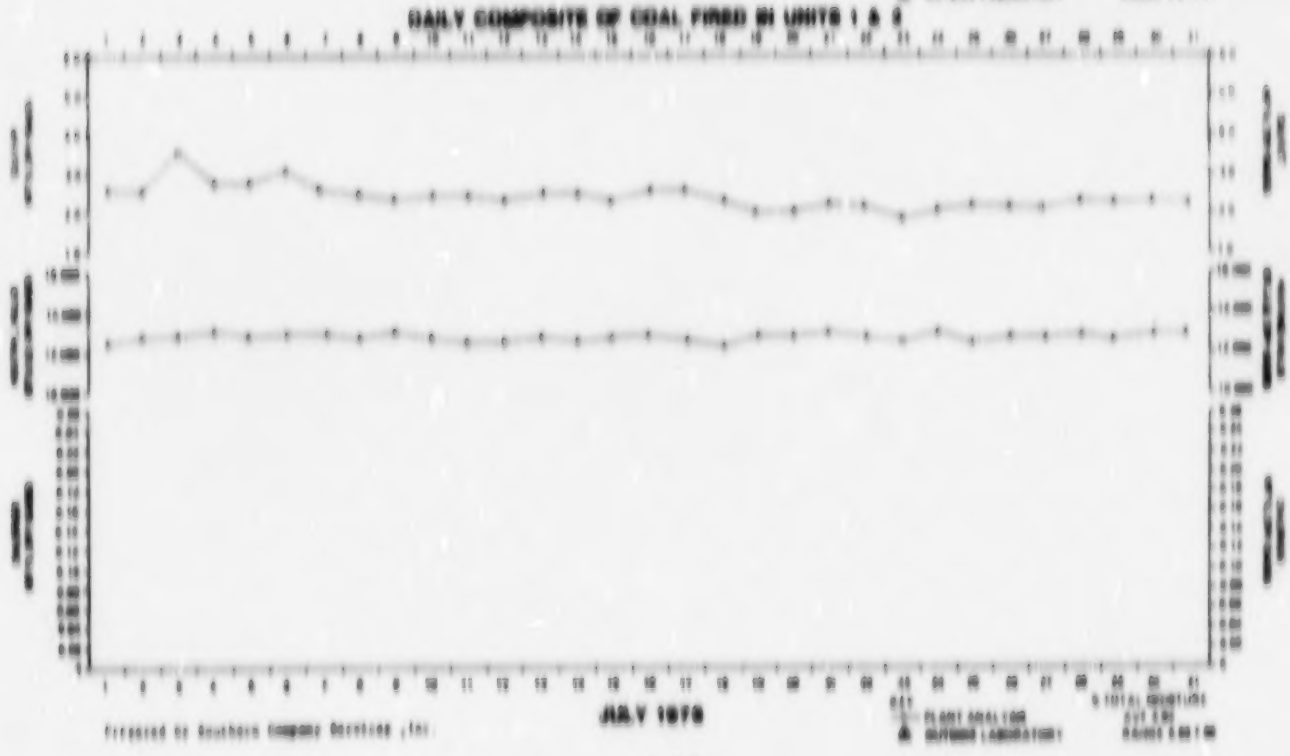
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JULY 1978

APPENDIX B

PROCESS AND BOILER OUTAGES

SYSTEM AND BOILER OPERATING HISTORY[1]
CEA / ADL DUAL ALKALI PROCESS

BOILER OUTAGES

CAUSE/EXPLANATION	PERIOD	DURATION (HRS)	NO.	MO.
[illegible]	[illegible]	[illegible]	[illegible]	FEB
[illegible]	[illegible]	[illegible]	[illegible]	FEB
[illegible]	[illegible]	[illegible]	[illegible]	MAR
[illegible]	[illegible]	[illegible]	[illegible]	MAR
[illegible]	[illegible]	[illegible]	[illegible]	APR
[illegible]	[illegible]	[illegible]	[illegible]	MAY
[illegible]	[illegible]	[illegible]	[illegible]	MAY
[illegible]	[illegible]	[illegible]	[illegible]	JUN
[illegible]	[illegible]	[illegible]	[illegible]	JUL
[illegible]	[illegible]	[illegible]	[illegible]	JUL
[illegible]	[illegible]	[illegible]	[illegible]	AUG

Prepared by Southern Company Services, Inc.

SYSTEM AND BOILER OPERATING HISTORY[1]
CEA / ADL DUAL ALKALI PROCESS

	PROCESS OUTAGES				
MO.	NO.	DURATION (HRS)	PERIOD		CAUSE/EXPLANATION
FEB	1	[illegible]	[illegible]	[illegible]	[illegible]
FEB	2	[illegible]	[illegible]	[illegible]	[illegible]
FEB	3	[illegible]	[illegible]	[illegible]	[illegible]
FEB	4	[illegible]	[illegible]	[illegible]	[illegible]
FEB	5	[illegible]	[illegible]	[illegible]	[illegible]
MAR	6	[illegible]	[illegible]	[illegible]	[illegible]
MAR	7	[illegible]	[illegible]	[illegible]	[illegible]
MAR	8	[illegible]	[illegible]	[illegible]	[illegible]
APR	9	[illegible]	[illegible]	[illegible]	[illegible]
APR	10	[illegible]	[illegible]	[illegible]	[illegible]
MAY	11	[illegible]	[illegible]	[illegible]	[illegible]
MAY	12	[illegible]	[illegible]	[illegible]	[illegible]
MAY	13	[illegible]	[illegible]	[illegible]	[illegible]
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JUN	15	[illegible]	[illegible]	[illegible]	[illegible]
JUL	16	[illegible]	[illegible]	[illegible]	[illegible]
JUL	17	[illegible]	[illegible]	[illegible]	[illegible]
JUL	18	[illegible]	[illegible]	[illegible]	[illegible]
JUL	19	[illegible]	[illegible]	[illegible]	[illegible]
AUG	20	[illegible]	[illegible]	[illegible]	[illegible]

Prepared by Southern Company Services, Inc.

SYSTEM AND BOILER OPERATING HISTORY[1]
CEA / ADL DUAL ALKALI PROCESS

(Continued)

BOILER OUTAGES

CAUSE/EXPLANATION	PERIOD	DURATION (HRS)	NO.	MO.
[illegible]	[illegible]	[illegible]	[illegible]	SEP
[illegible]	[illegible]	[illegible]	[illegible]	
LOAD ORDERS	[illegible]	[illegible]	[illegible]	
UNIT 5/6 1 1/8 FAN FAILURE [illegible]	[illegible]	[illegible]	11	OCT
LOAD ORDERS	[illegible]	[illegible]	[illegible]	NOV
				DEC
5 YEAR TURBINE INSPECTION	[illegible]	[illegible]	[illegible]	JAN 76
[illegible] AND GOVERNOR VALVE	[illegible]	[illegible]	[illegible]	FEB

Prepared by Southern Company Services, Inc.

SYSTEM AND BOILER OPERATING HISTORY[1]
CEA / ADL DUAL ALKALI PROCESS

Continued

MO.		PROCESS OUTAGES NO.	DURATION (HRS)	PERIOD		CAUSE / EXPLANATION
SEP	[redacted]					
		16	89.50	9/25/75 2130	9/29/75 1900	BOILER DOWN FOR LOAD ORDERS
		17	115.00	9/30/75 1900	10/1/75 1100	BOILER DOWN ID FAN FAILURE. BOILER WAS NOT AVAILABLE TO THE PROCESS UNTIL 1900 ON 10/1/75 DUE TO TRANSFORMER PROBLEMS IN THE PLANT
OCT	[redacted]					
NOV	[redacted]	18	184.00	11/23/75 0900	12/1/75 0500	HOLE IN FIRST STAGE REACTOR BOTTOM CAUSED BY FEED LIQUOR ENTRANCE BEING TOO CLOSE TO TRAY BOTTOM. THE ENTIRE REACTOR DESIGN CHANGED DURING JANUARY OUTAGE BY THE TEST
DEC	[redacted]					
JAN 76	[redacted]	19	1005.50	1/12/76 2300	2/12/76 0830	BOILER WAS SHUT DOWN FOR FIVE YEAR TURBINE INSPECTION. MAJOR REPAIRS AND MODIFICATIONS TO ST WERE PERFORMED BY GE FOR TEST
FEB						

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SYSTEM AND BOILER OPERATING HISTORY[1]
CEA / ADL DUAL ALKALI PROCESS

Continued

BOILER OUTAGES				
CAUSE/EXPLANATION	PERIOD	DURATION (HRS)	NO.	MO.
REMOVED CEA BLANK FROM FLUE GAS DUCT	3/10/78 1056 3/10/78 1241	1.75	77	MAR
[1] EXPLANATION FOR PROCESS OUTAGE NO. 78 (BOILER ON LINE)	4/25/78 0130 4/28/78 1130	73.67	77	APR
CLEANED LIGHT OIL FROM AIR PREHEATER	5/22/78 0955 5/23/78 0333	5.73	78	MAY
ECONOMIZER TUBE LEAK	6/10/78 0044 6/11/78 0845	21.60	79	JUN
[2] INSTALL SAMPLING NOZZLE IN INLET DUCT (BOILER ON LINE)	6/19/78 0800 6/19/78 1547	7.78	80	JUN
				JUL

7/20/1978

Prepared by Southern Company Services, Inc.

SYSTEM AND BOILER OPERATING HISTORY[1]
CEA / ADL DUAL ALKALI PROCESS

Continued

PROCESS OUTAGES

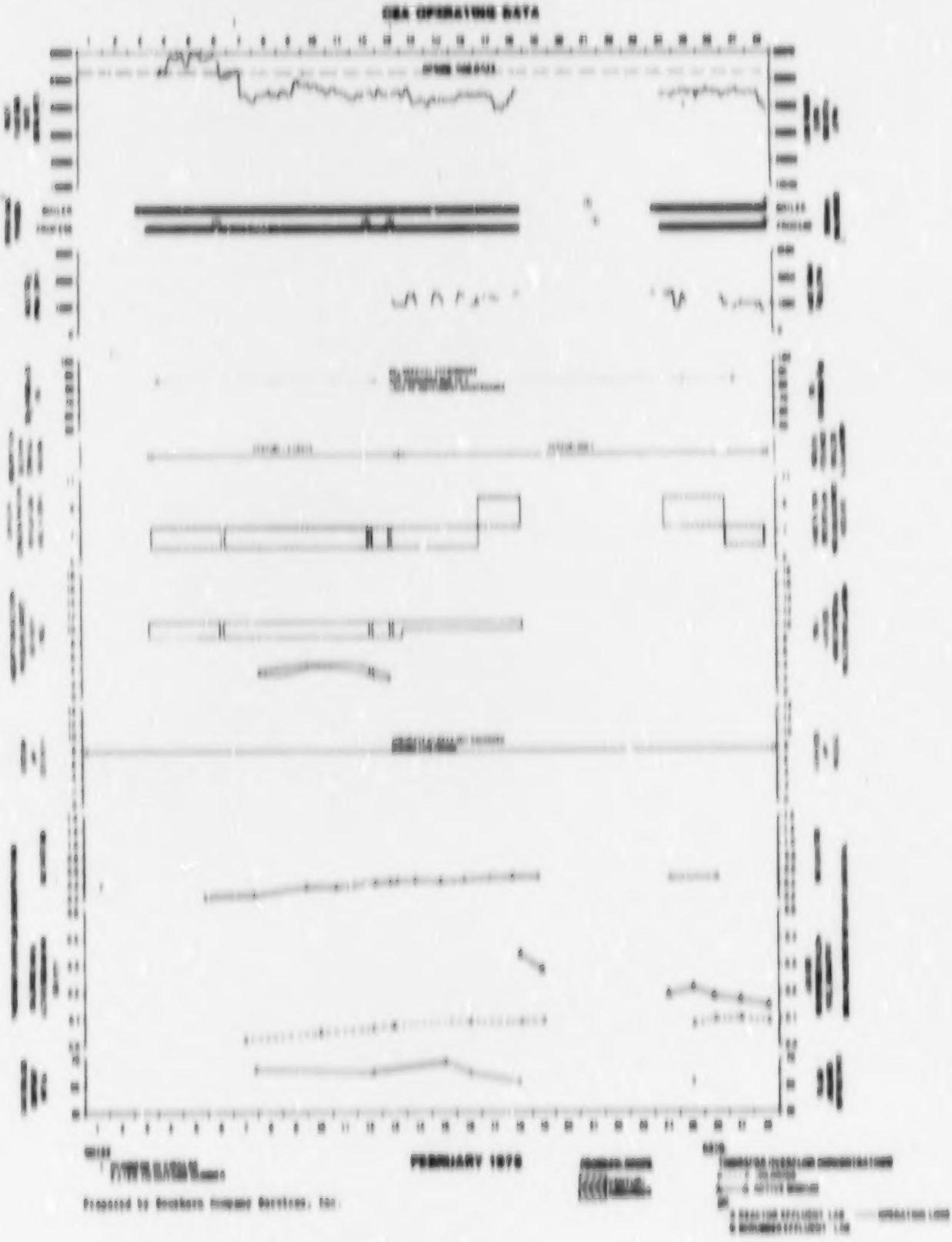
MO.	NO.	DURATION (HRS)	PERIOD	CAUSE/EXPLANATION
MAR	20	0.58	3/10/75	3/10/75 1110 BROKEN LINE TO REACTOR FROM VENTURI (CORRODED BOLTS)
	21	15.05	3/21/75 1310	3/22/75 1521 BROKEN COUPLING ON REACTION TANK AGITATOR (WELDED)
	22	0.13	3/29/75 0854	3/29/75 0906 INSTALLED SAMPLE PORTS ON FLUE GAS INLET DUCT
APR	23	20.50	4/9/75 1530	4/10/75 1800 AGITATOR SHAFT BROKE AT NEW WELD (SEE OUTAGE 21)
	24	1.13	4/10/75 1685	4/10/75 2115 UNIT PRECIPITATOR DOWN MATERIAL BALANCE PERIOD IN PROGRESS. THEREFORE SHUT DOWN TO KEEP PARTICULATES OUT OF THE SYSTEM
	25	79.87	4/20/75 0730	4/25/75 1145 FLAKT TRANSFORMER OUT. POWER AVAILABLE AGAIN AT 1105
MAY	26	61.00	5/18/75 0500	5/21/75 1800 REACTOR AGITATOR COUPLING BROKE AT PREVIOUS WELD (SEE OUTAGE 23). MACHINIST NOT AVAILABLE UNTIL 5/21/75 AT 0800. OUTAGE AFTER 1000 ON 5/18/75 DUE TO LACK OF BOILER PLANT
	27	8.50	5/23/75 0030	5/23/75 1100 UNIT NO. 1 DOWN TO CLEAN AIR HEATER
	28	2.25	5/28/75 1215	5/28/75 1430 REPLACE REACTOR BLEED CONTROL VALVE. RUBBER LINED FLOW FAILED. SEE NOTE FOR OUTAGE 29
	29	1.33	5/28/75 1500	5/28/75 1730 ALUMINUM SCREEN LINING UNIT THAT WAS INSTALLED IN AN UNSPECIFIED LOCATION IN THE VENTURI (ADL) LOOSE AND PASSED THROUGH THE VENTURI PUMP. DESTROYED THE PUMP IMPELLER AND IMPELLER
JUN	30	3.75	6/6/75 0800	6/6/75 1565 LEVEL CONTROL PROBLEMS. FOUND ABSORBER PUMP SEAL WATER HOSE OPEN. CORRECTED PUT SYSTEM BACK ON LINE
	31	0.75	6/9/75 1100	6/9/75 1565 SAME PROBLEM AS OUTAGE 30. ALL LOOSE MATERIAL REMOVED FROM VENTURI
	32	1.50	6/9/75 0500	6/9/75 1030 CLOGGED INLINE SO2 ANALYZER FILTERS. PROBE IS LOCATED AT A FAN DISCHARGE (A HIGH GAS VELOCITY). OUTAGE WOULD NOT HAVE BEEN NECESSARY IF THE PROBE LOCATION WERE DIFFERENT
	33	32.83	6/10/75 0530	6/11/75 1565 BOILER INSPECTION (ECONOMIZER TUBE LEAK)
	34	20.58	6/11/75 1800	6/13/75 1430 SCRUBBER LEVEL CONTROL VALVE STICKING (METAL TO METAL FILED & PUT BACK IN SERVICE)
	35	1.13	6/18/75 0900	6/18/75 1500 INSTALL SAMPLING SUPPLY ON INLET DUCT
	36	18.83	6/18/75 1711	6/19/75 1530 UNIT TO DISPATCHER'S OFFICE. SPRAY PUMPS REPLACED
			7/3/75 0430	FINAL SHUTDOWN
JUL				

NOTES:
1 DATA ARE AS INDICATED THROUGH IN SERVICE
LIGHT AREAS INDICATE THROUGHOUT OF SERVICE
2 ALTHOUGH THE BOILER WAS ON LINE IT WAS NOT AVAILABLE TO THE PROCESS AS INDICATED
3 [illegible]

Prepared by Southern Company Services, Inc.

APPENDIX C

PROCESS OPERATING DATA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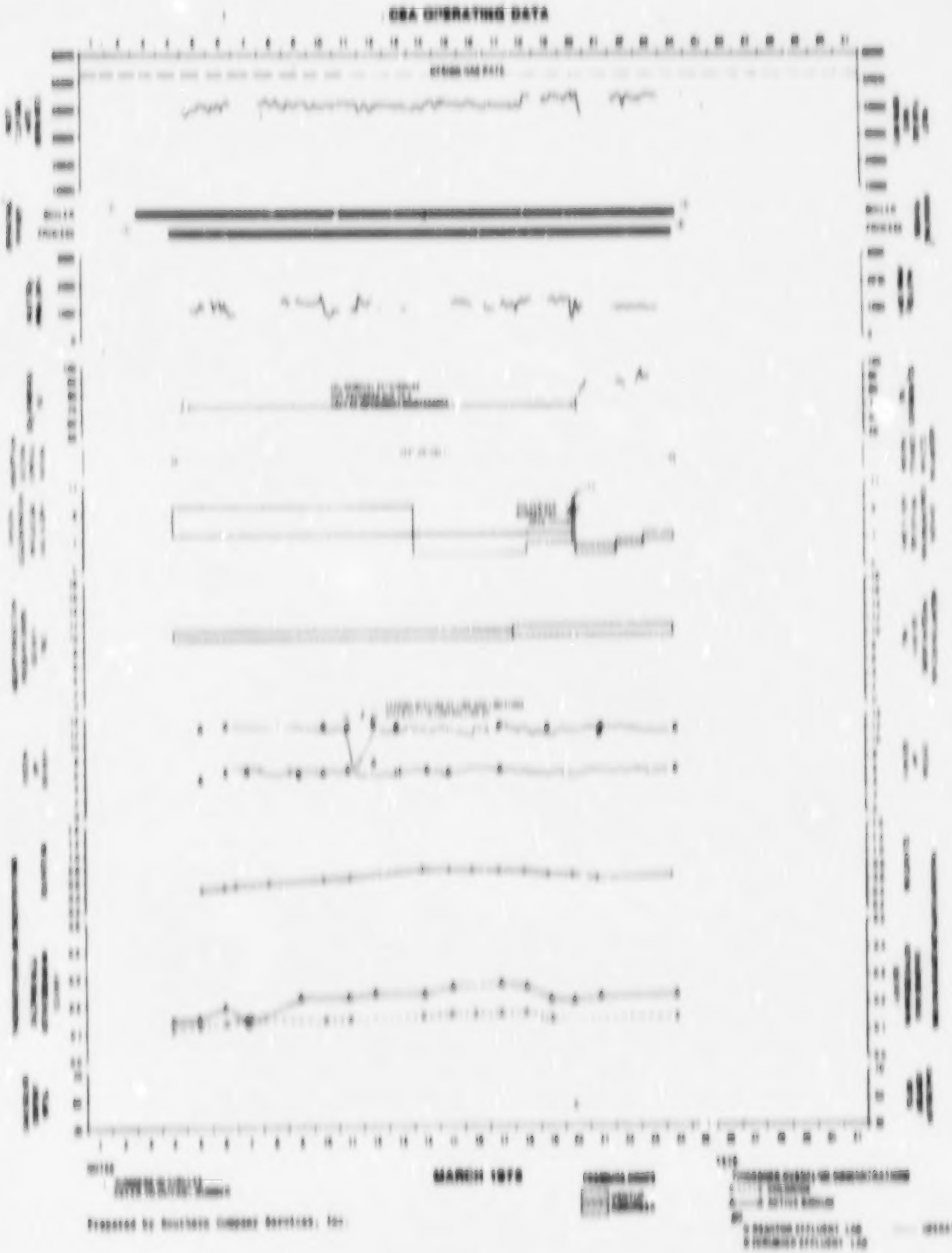
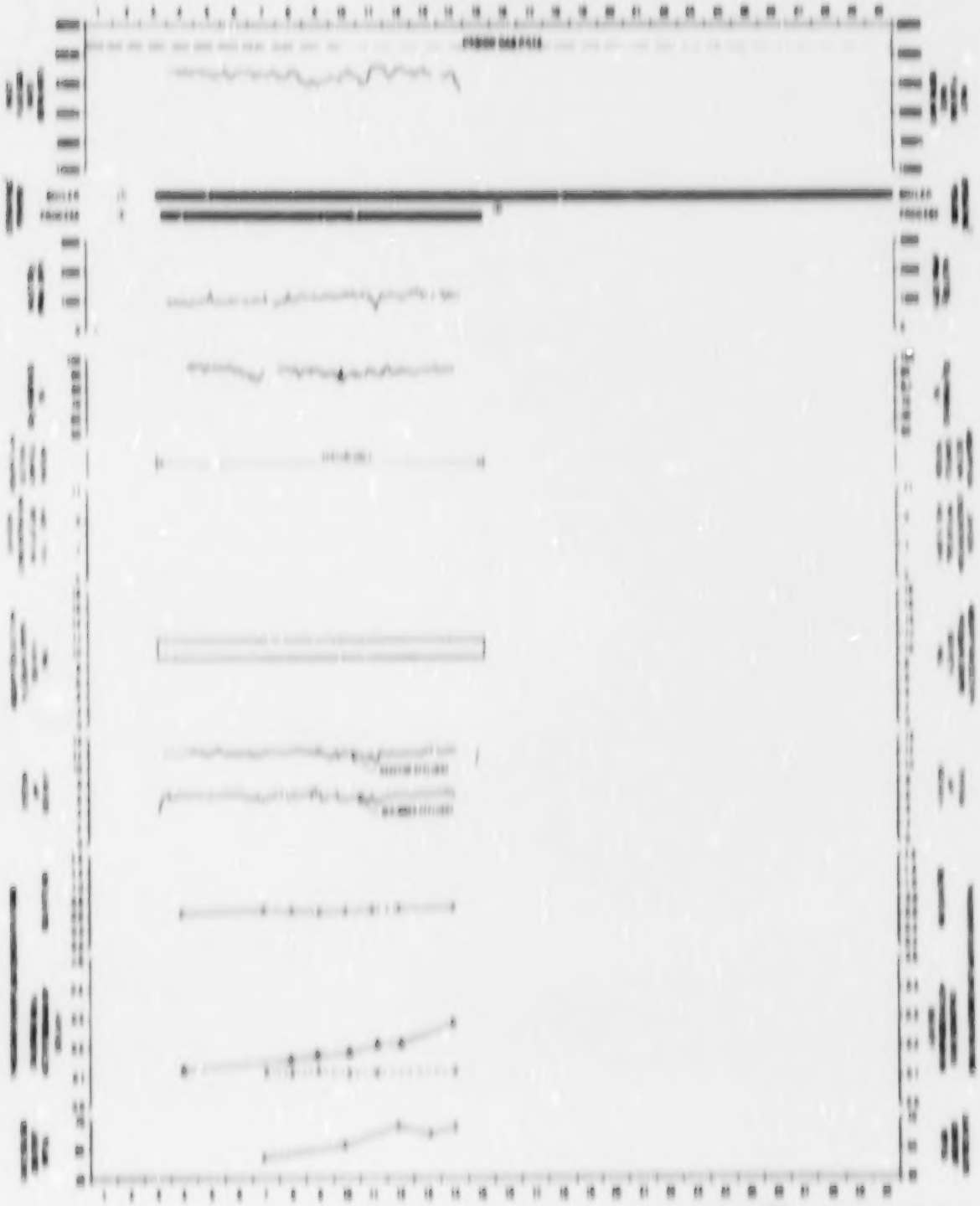
FEBRUARY 1978
Prepared by Brookhaven Computer Services, Inc.


CBA OPERATING DATA
MARCH 1978

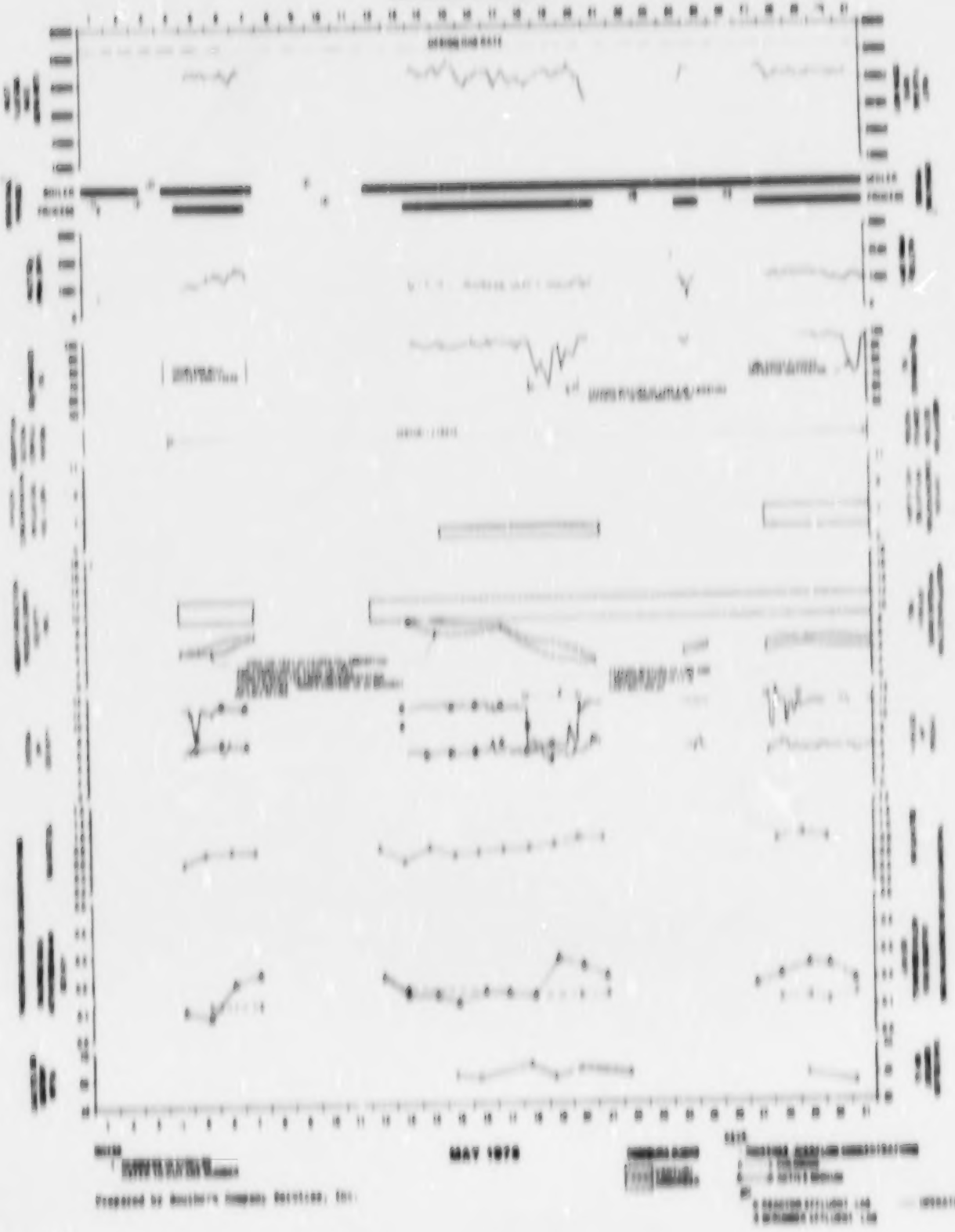
CBA OPERATING DATA



APRIL 1978

Prepared by Southern Company Services, Inc.

CEA OPERATING DATA



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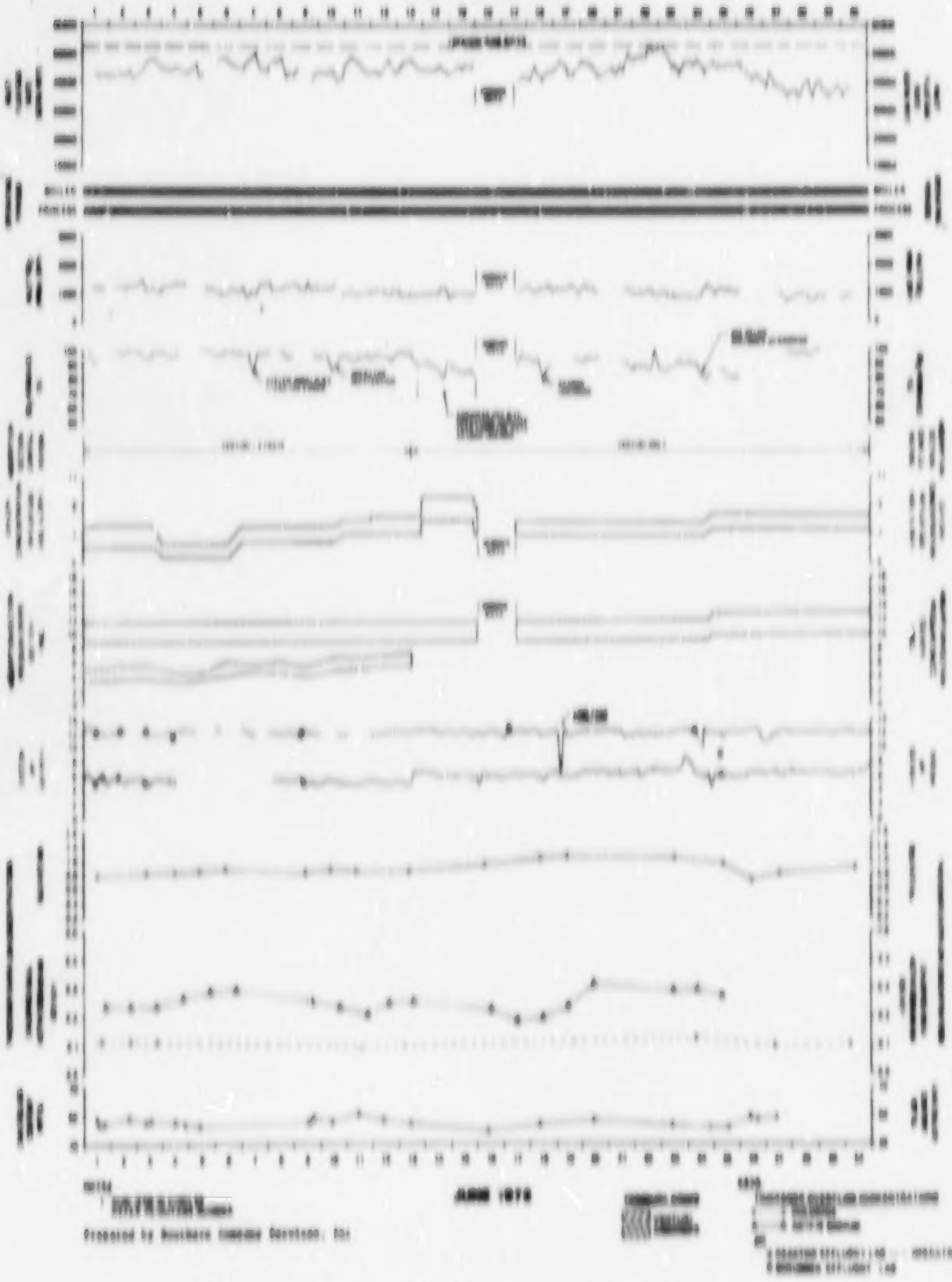

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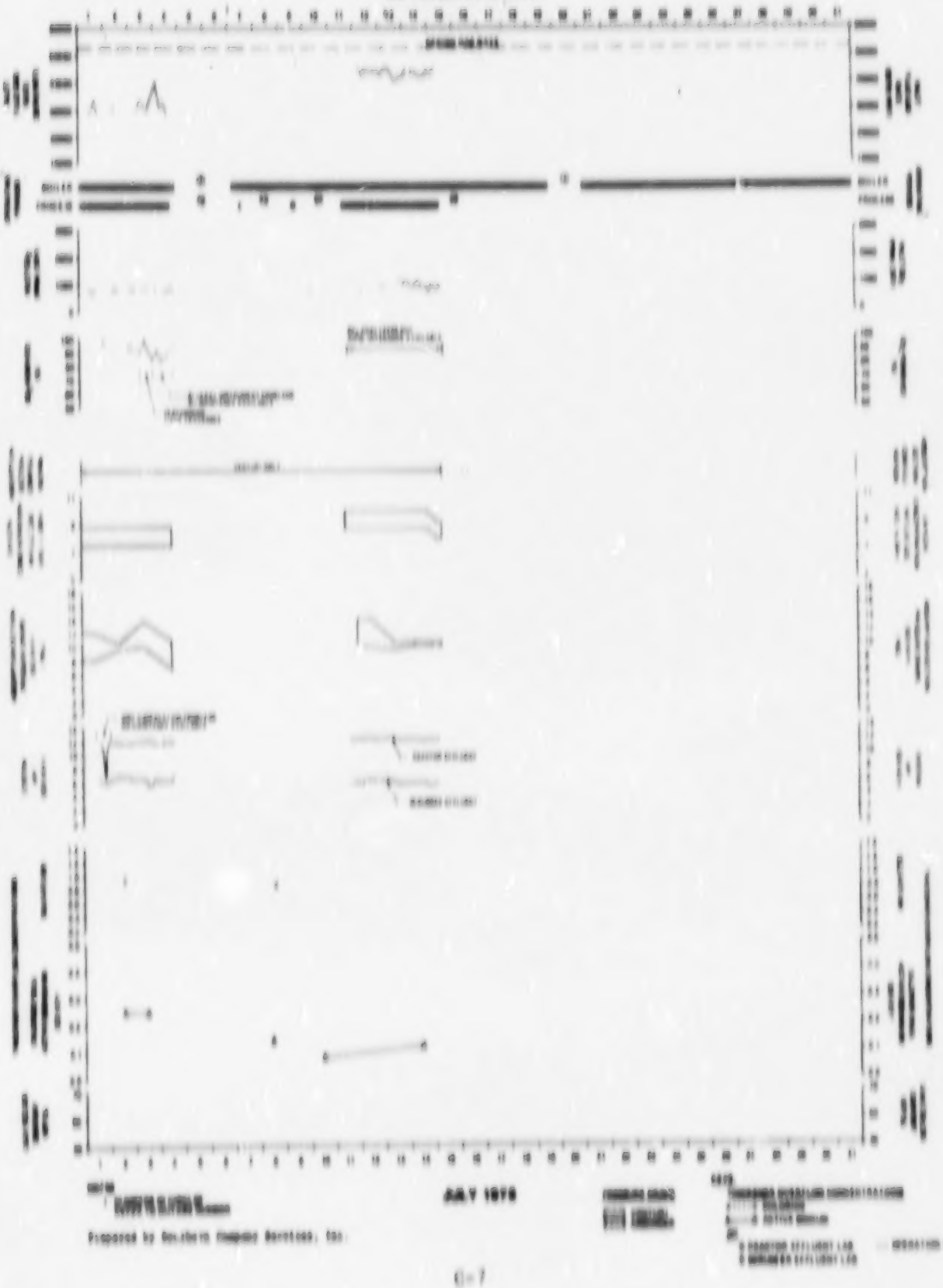
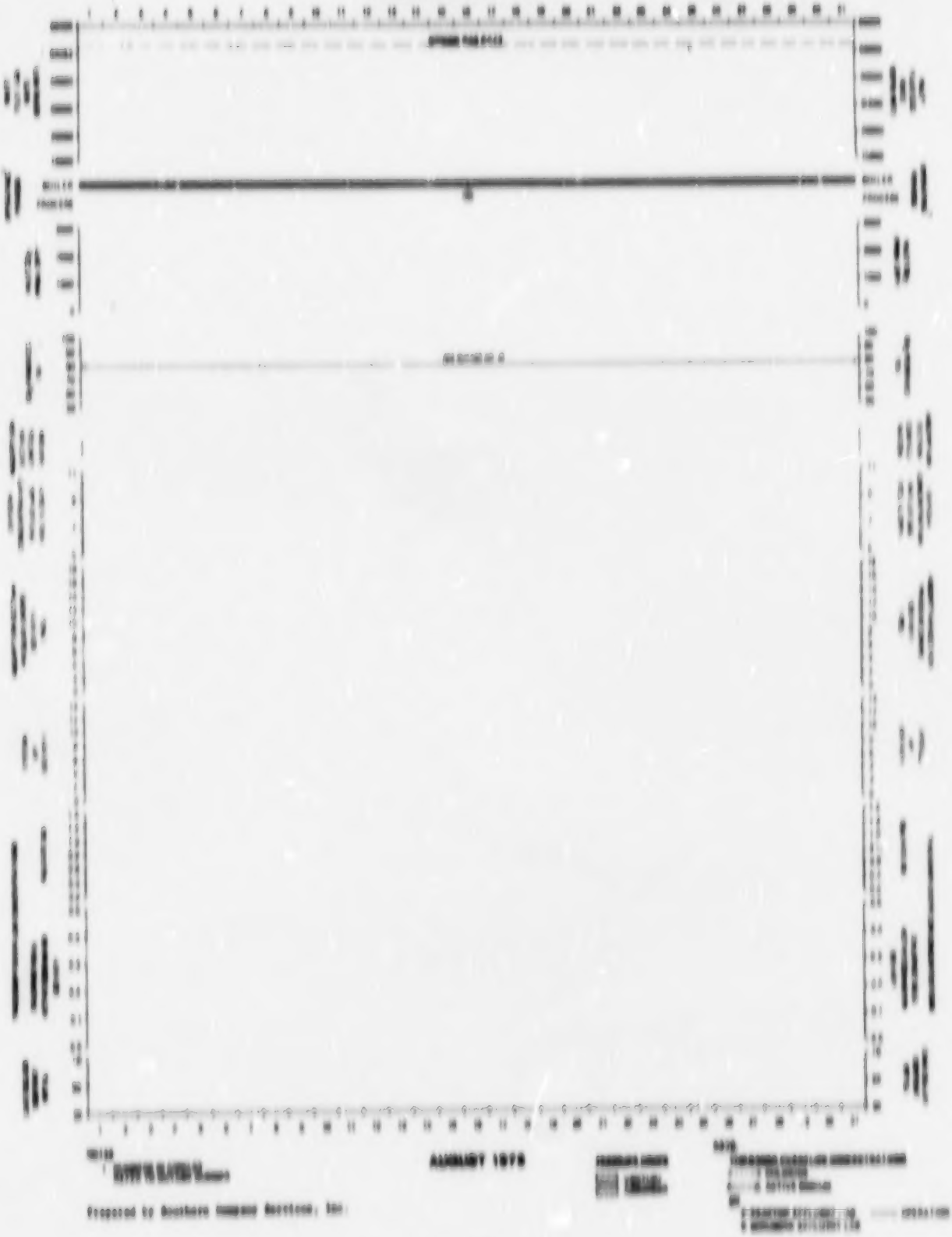


JULY 1978

Prepared by Gilbert Commercial Services, Inc.

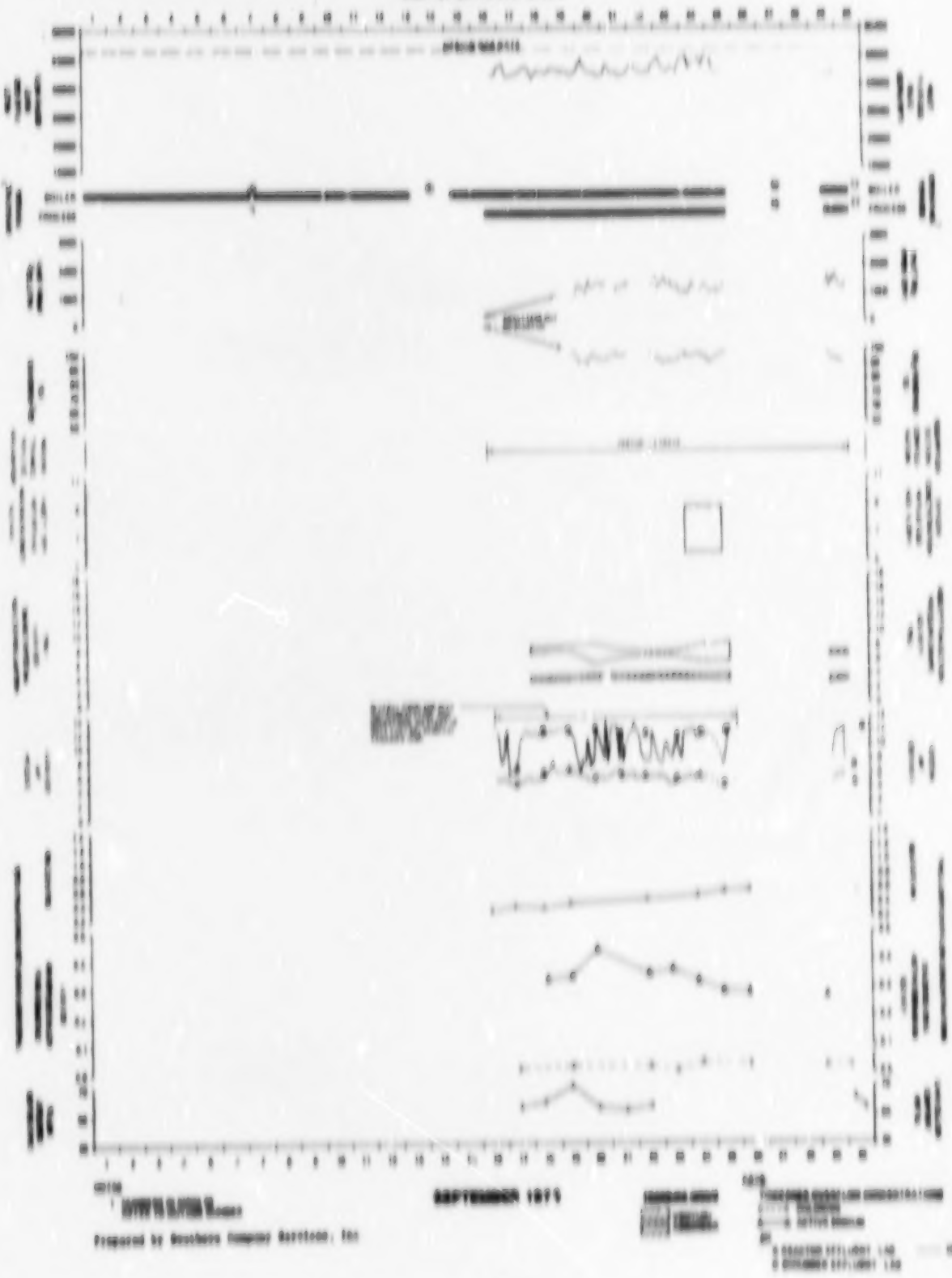
CRA OPERATING DATA



AUGUST 1978

Prepared by Southern Company Services, Inc.

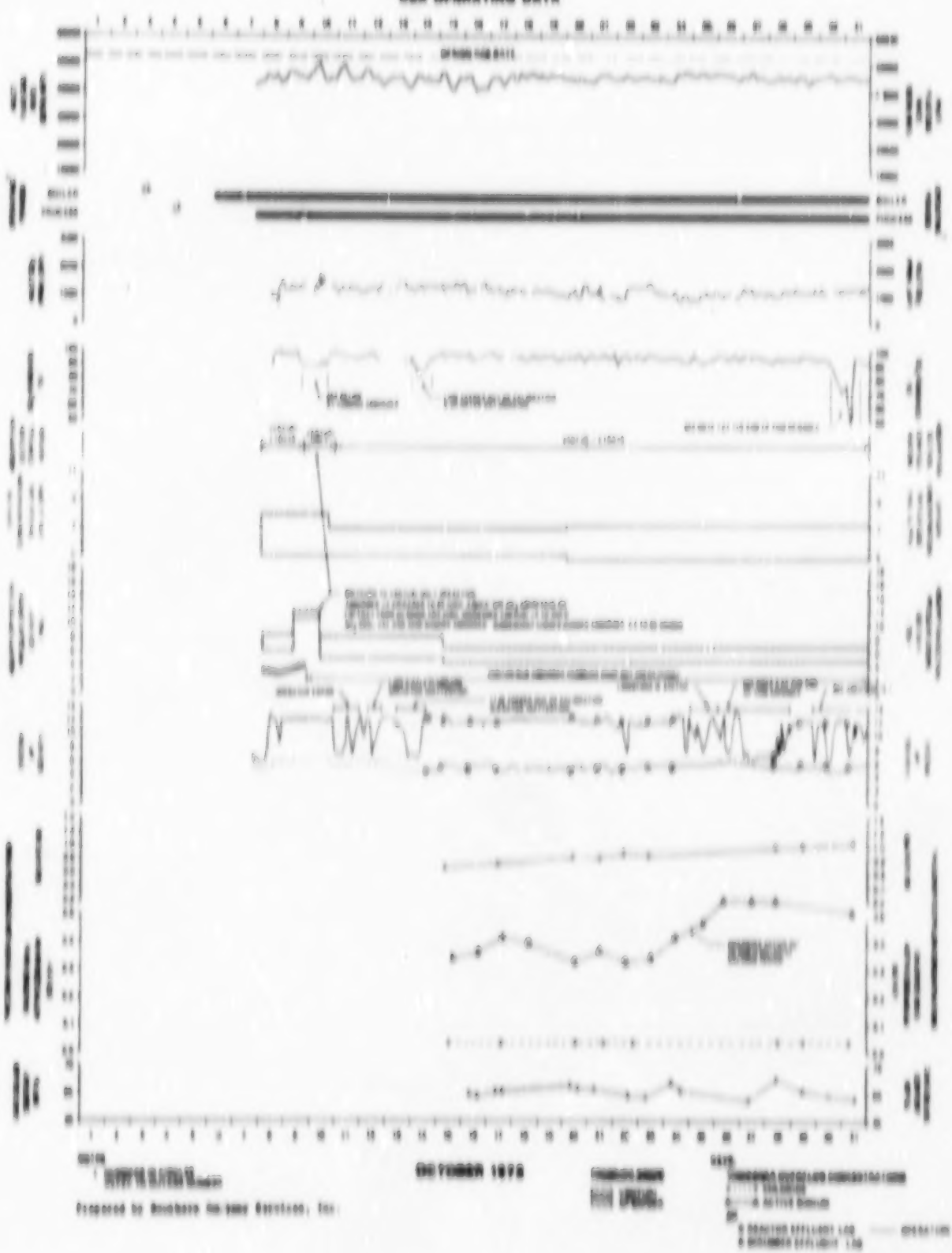
CEA OPERATING DATA



SEPTEMBER 1979

Prepared by Southern Company Services, Inc.

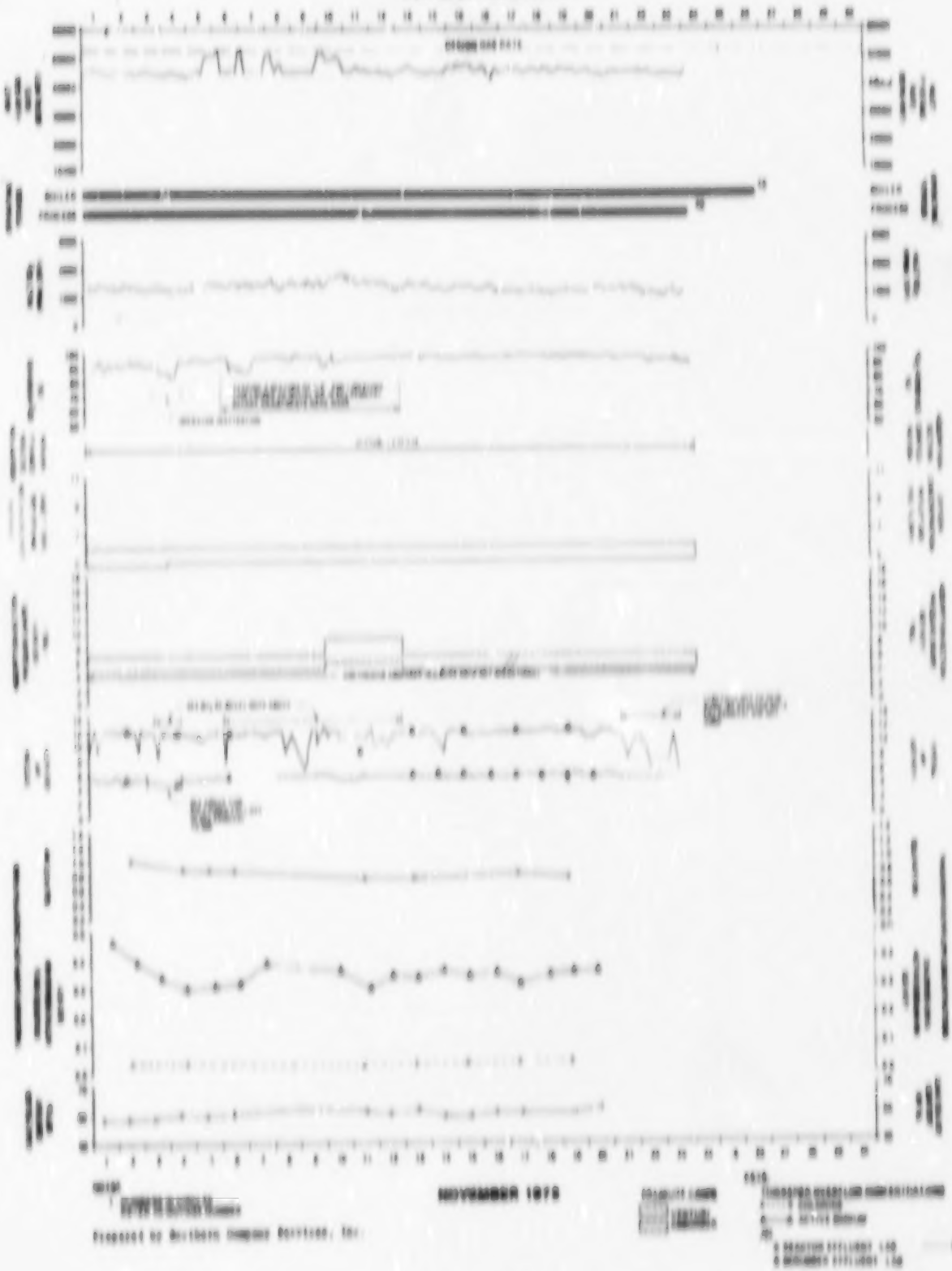
CRA OPERATING DATA



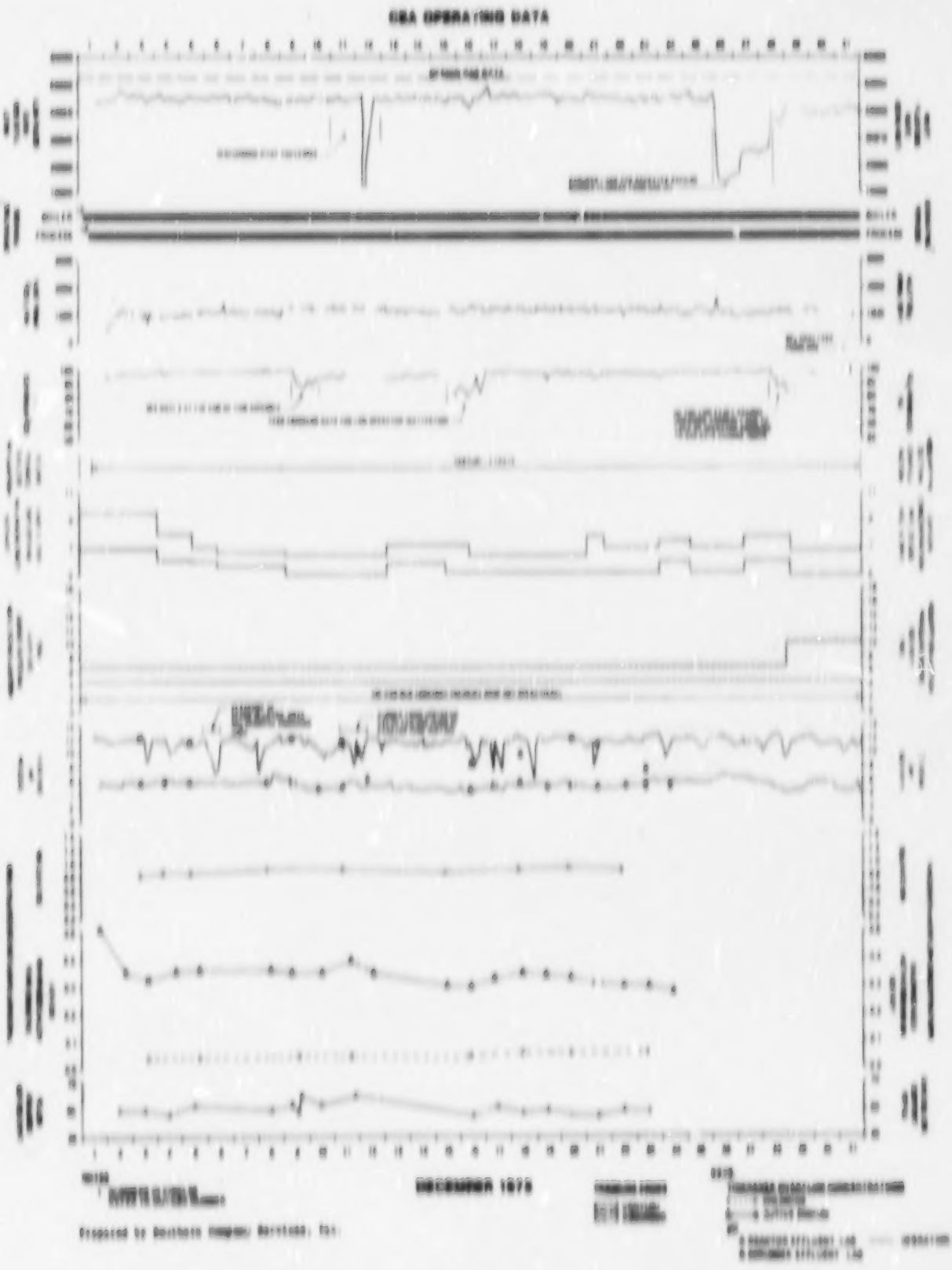
OCTOBER 1978

Prepared by Stockton Savings Services, Inc.

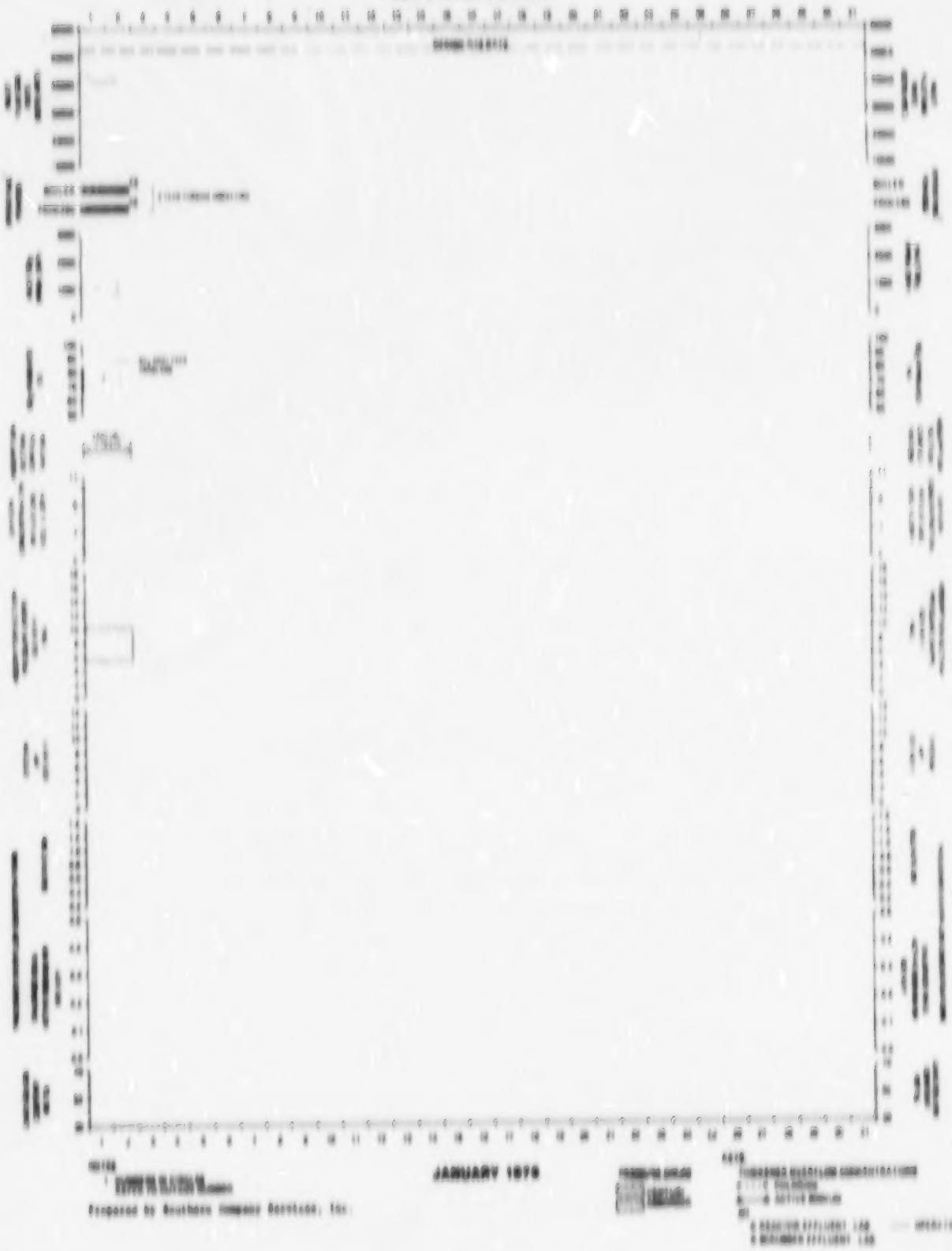
EBA OPERATING DATA



NOVEMBER 1979

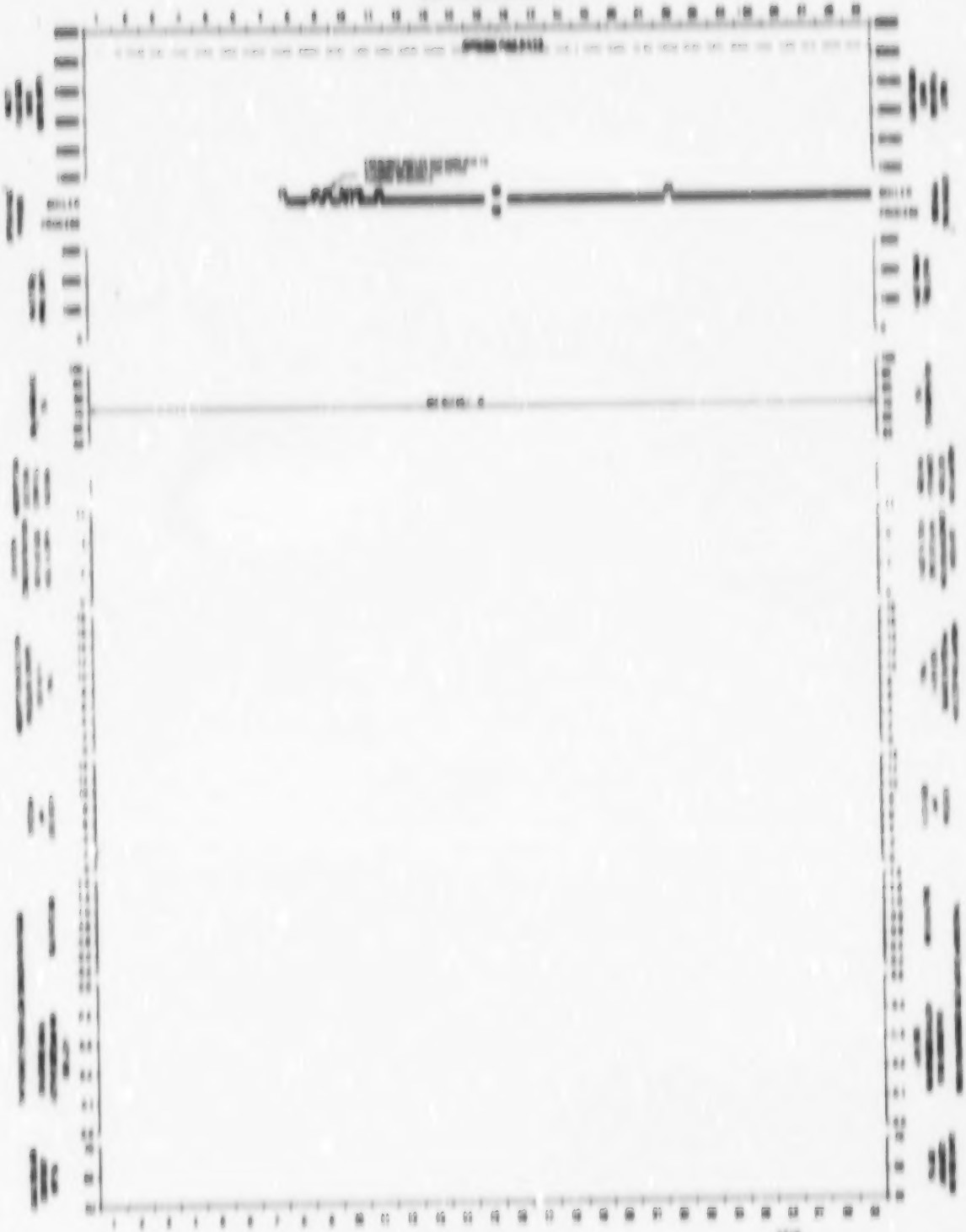

CBA OPERATING DATA
DECEMBER 1978

CBA OPERATING DATA



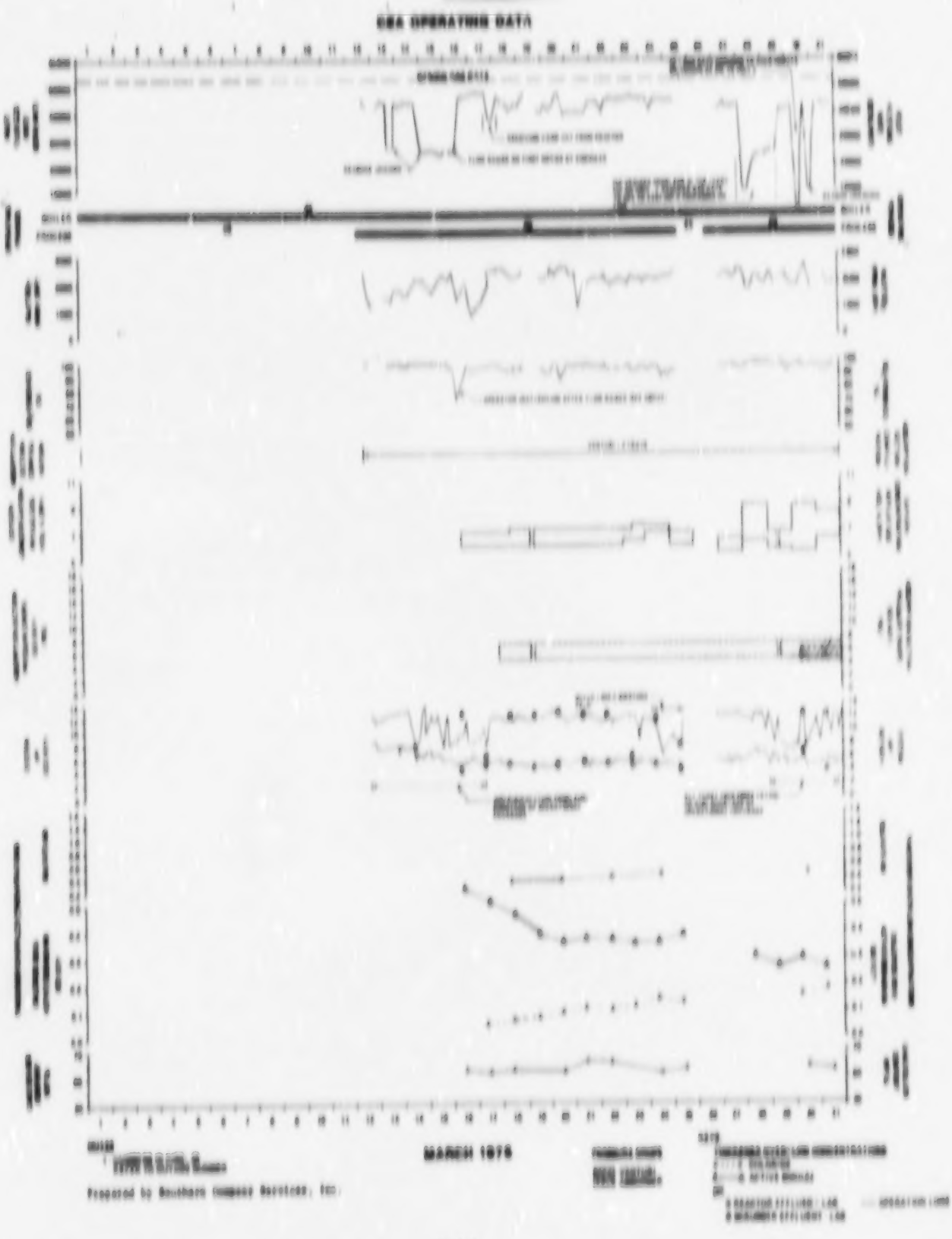
JANUARY 1978

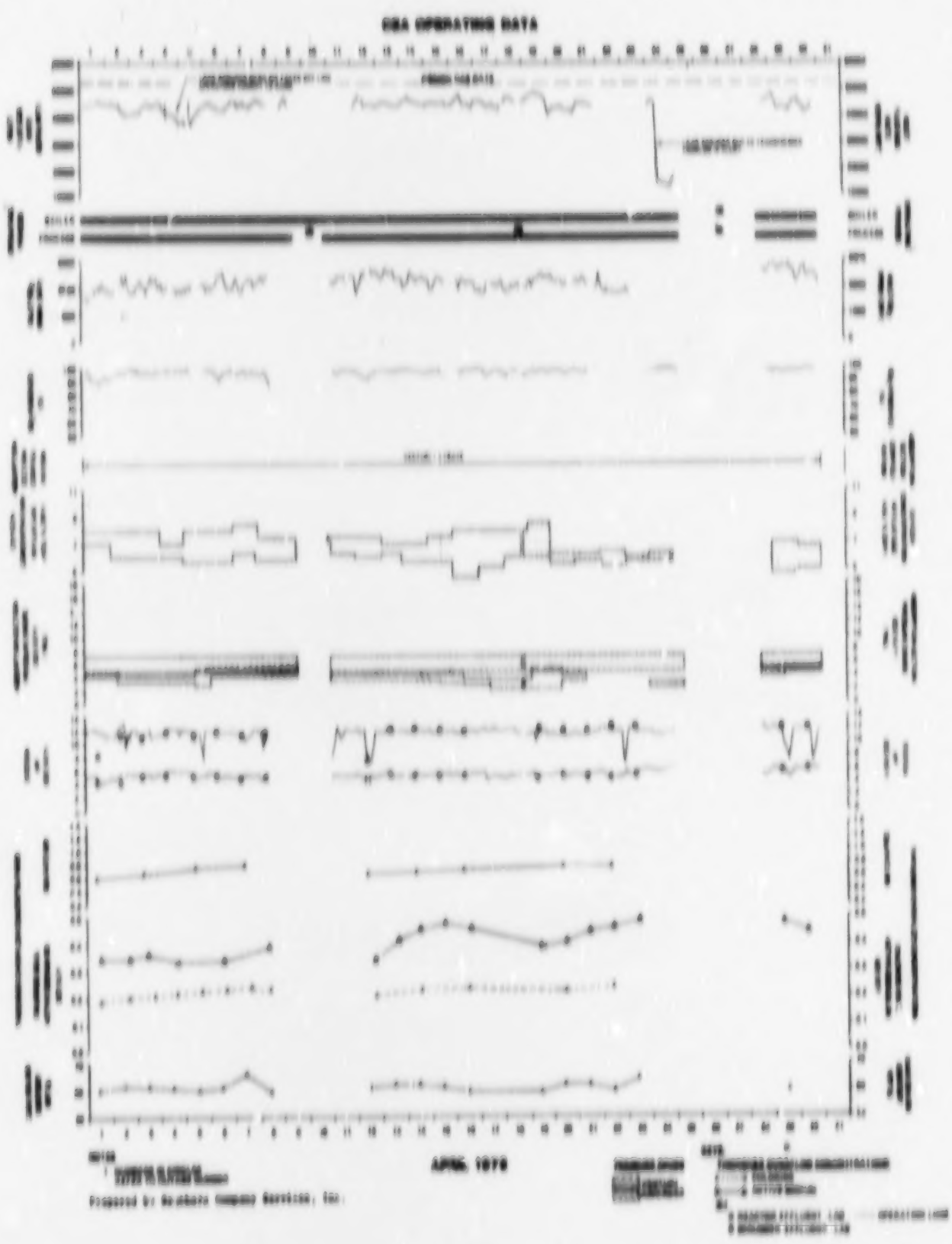
Prepared by Southern Company Services, Inc.

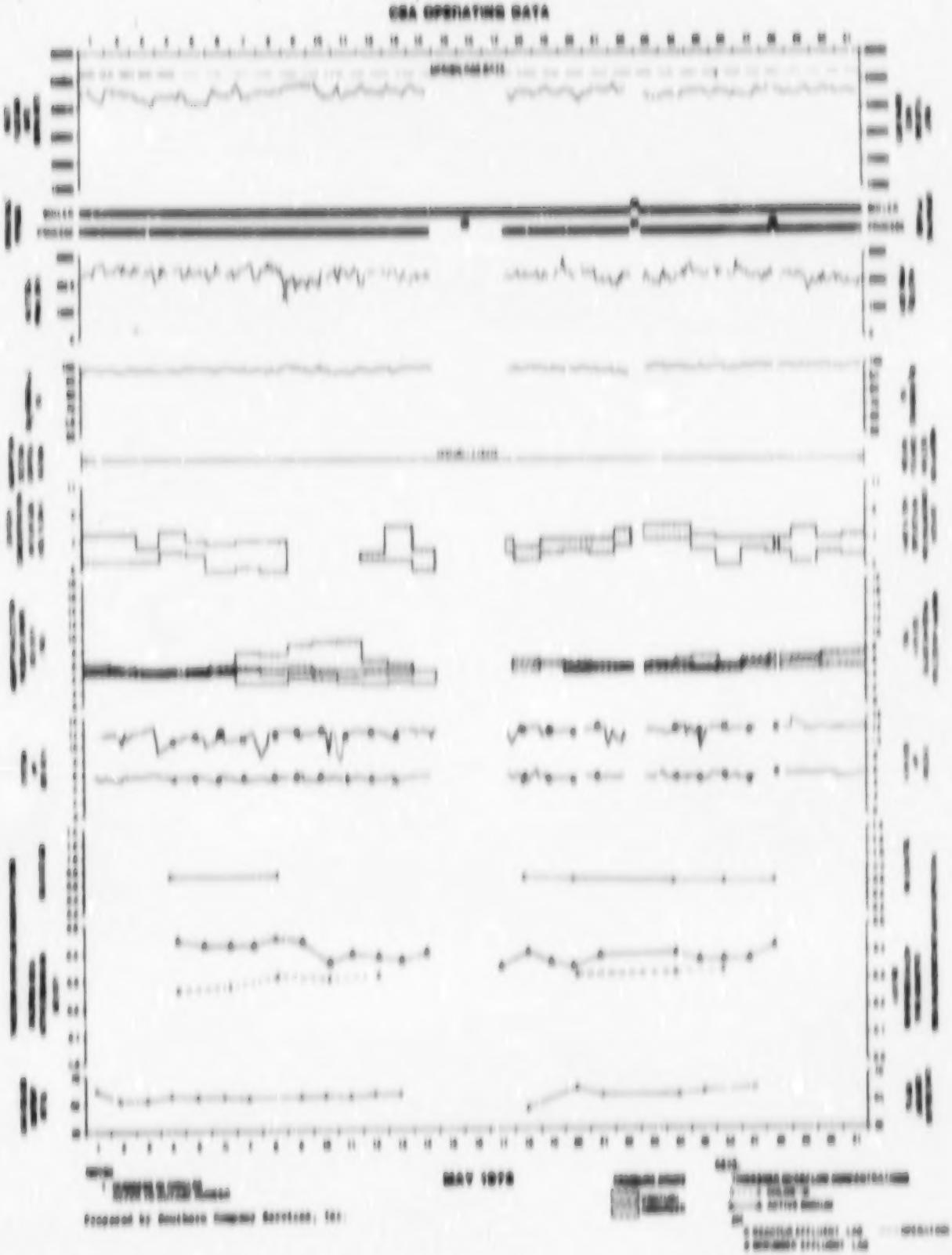


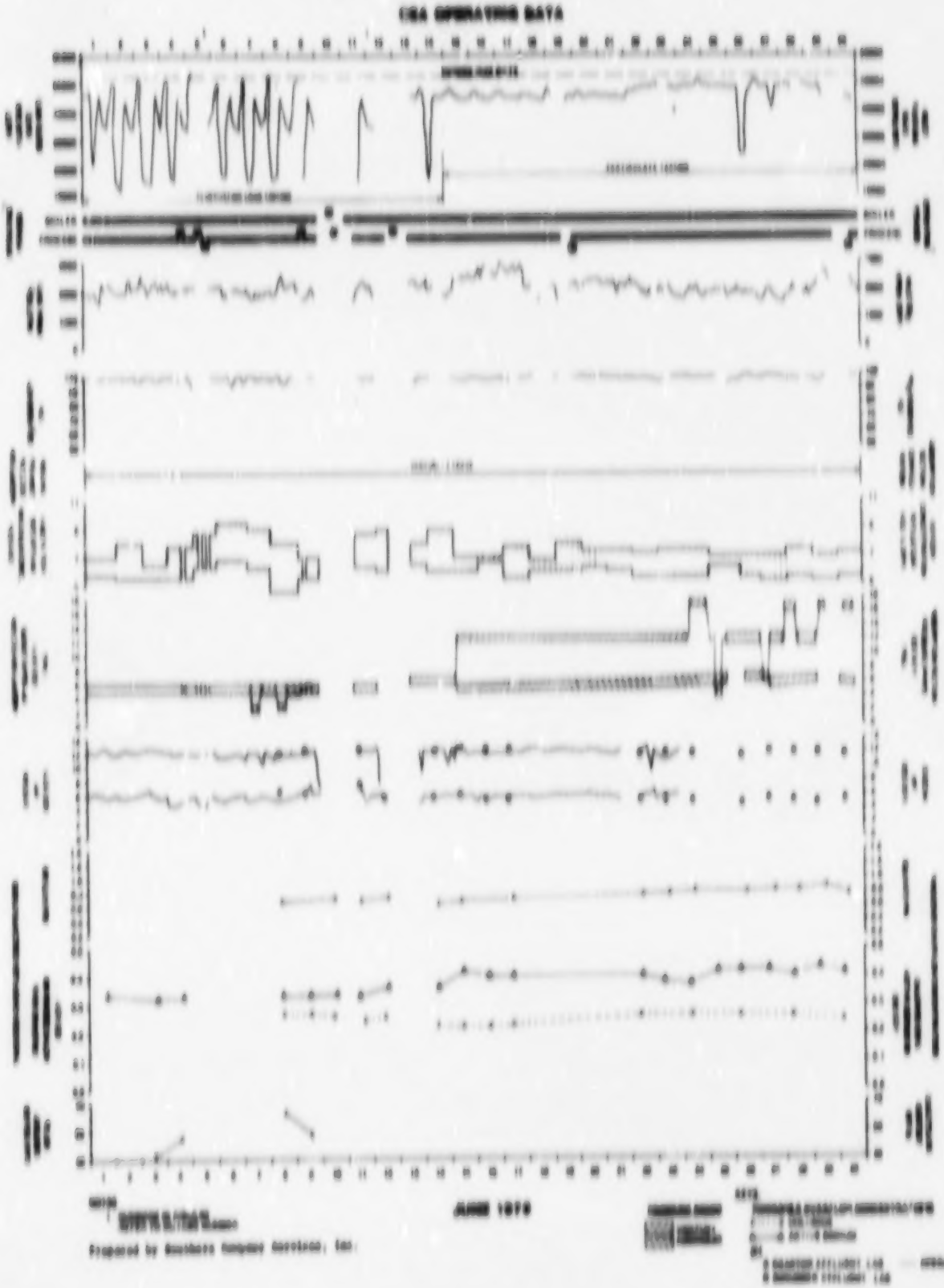
FEBRUARY 1978

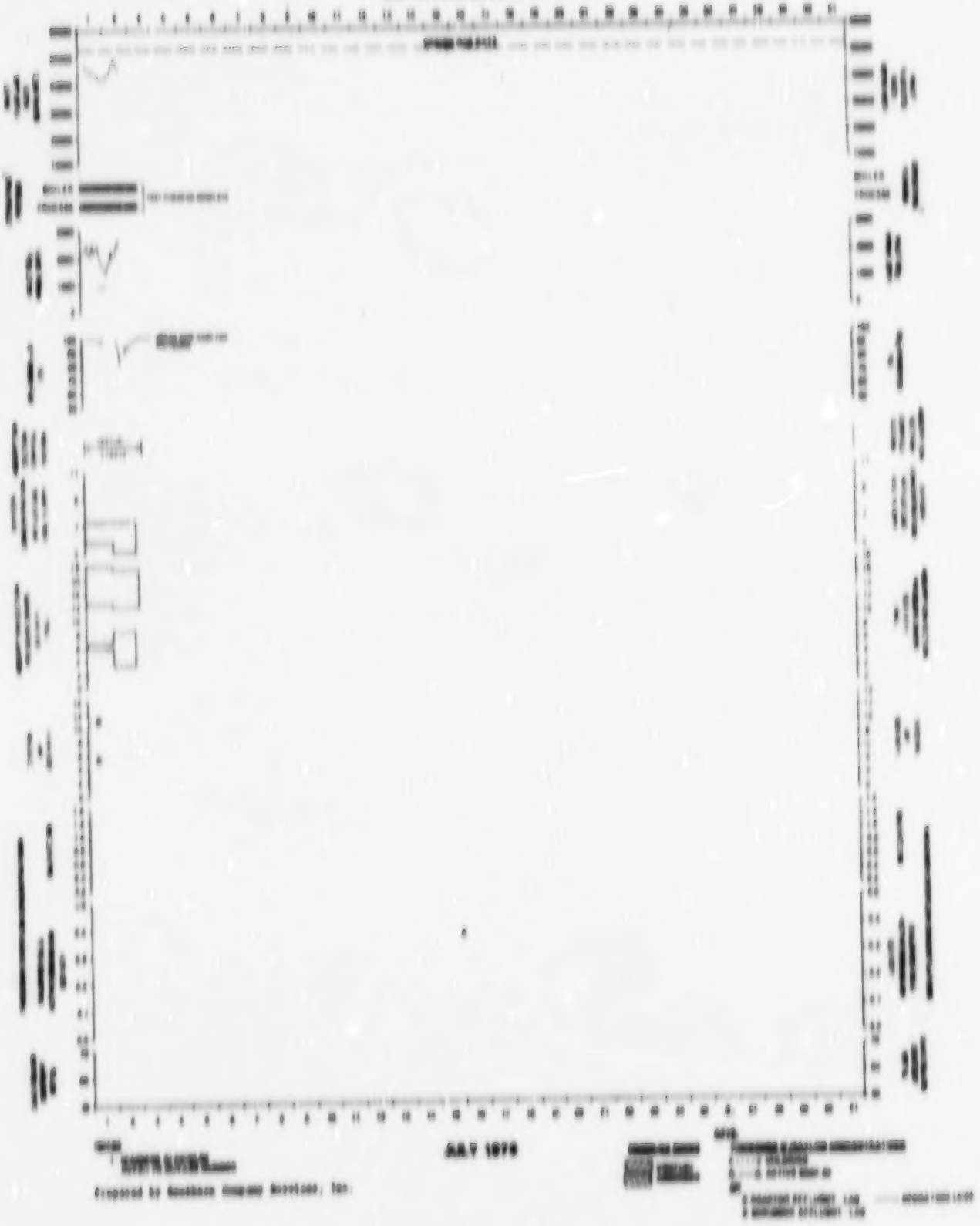
Prepared by Gruntons Computer Services, Inc.


CEA OPERATING DATA
MARCH 1976
Prepared by Southern Company Services, Inc.


EBA OPERATING DATA
APRIL 1978


CBA OPERATING DATA
MAY 1978


CRA OPERATING DATA
JUNE 1979
Prepared by Southern Company Services, Inc.



JULY 1976

APPENDIX D

TYPICAL PROCESS FLOWS AND STREAM COMPOSITIONS

[redacted]

[redacted]

[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
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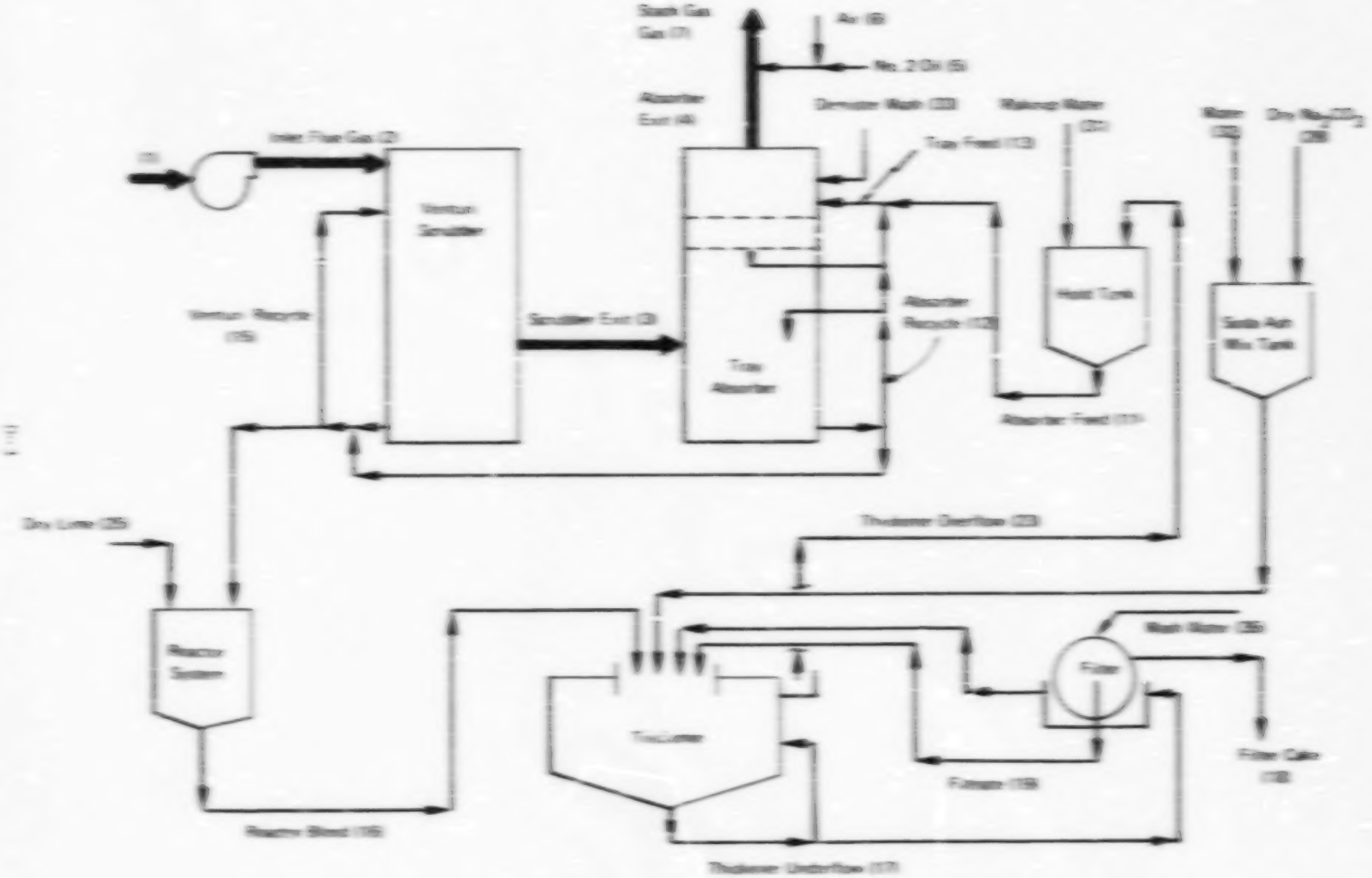

FIGURE 3-1 SYSTEM CONFIGURATION - JUNE 4, 1976 (RES-OD 1)

TABLE D-2

[illegible] COMPOSITION, DECEMBER 31, 1975 - (PERIOD 2)

[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

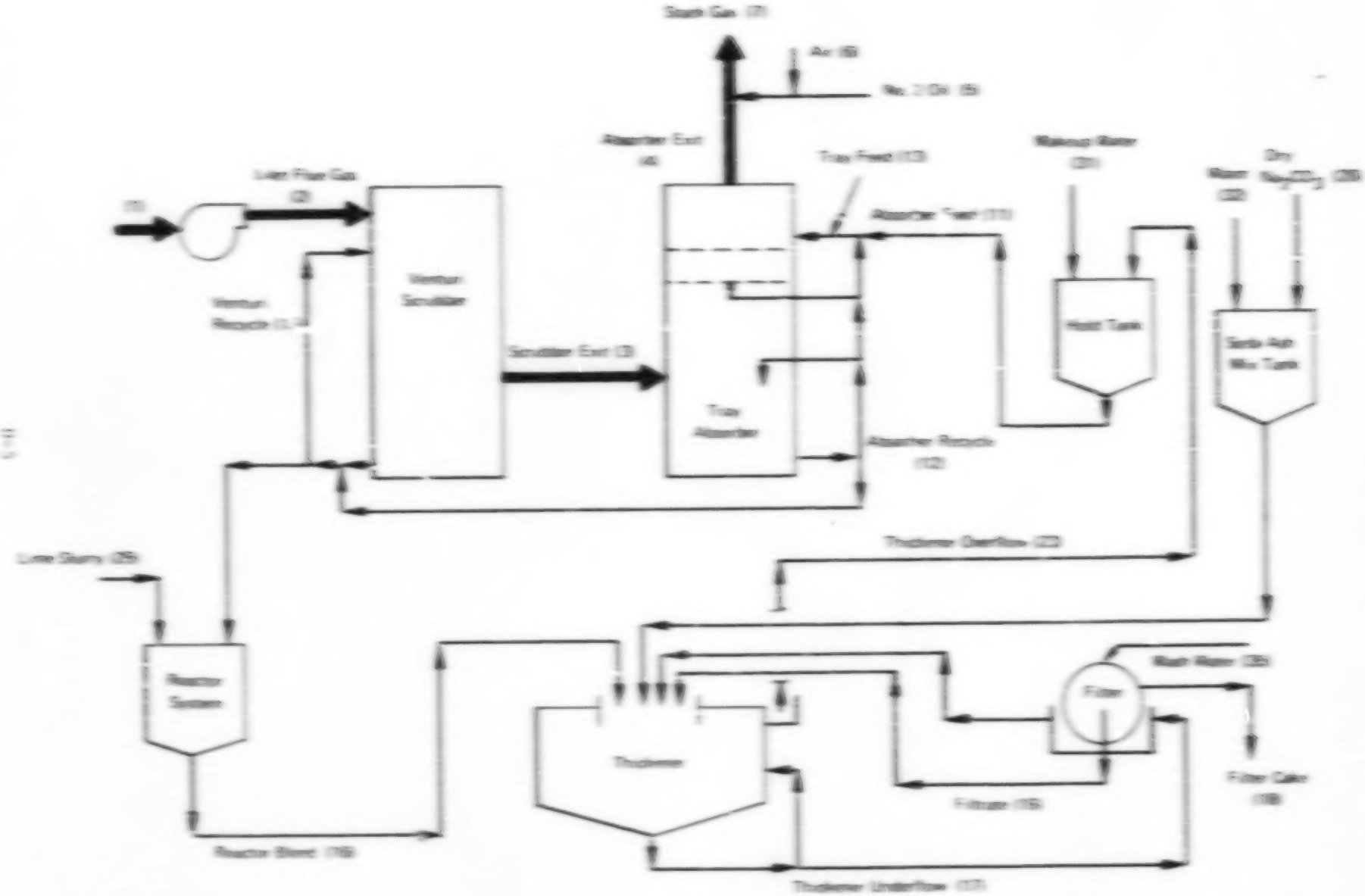

FIGURE D-2 SYSTEM CONFIGURATION--DECEMBER 20, 1975 (PERIOD 2)

TABLE I-3

STEAM COMPOSITION, MAY 12, 1976 - (PERIOD 3)

	1	2	4	7
HP STEAM				
Location	Flow Rate	Scrubber Inlet	Absorber Inlet	Reheated Gas
Flow Rate - lb/hr	45,000	—	—	—
Temperature (°F)	850-900	149	139	171
SO_2 (ppm)	2400	—	—	1177 ppm
H_2O (Vol. %)	— —	—	—	—
Pressure Drop (Psi)	— —	— —		
	1,144	5.0		
LOOP STEAM	11	12	13	15
Location	Absorber Feed	Absorber Recycle	Flue Gas Feed	Scrubber Recycle
Flow Rate - Lbs/Hr or Gal/Min	135-175	2400	265-295	1700
Composition:				
Σ Insoluble Solids	0	0	0	0
Liquid Analysis (M):				
Ca^{++}	0.45	—	—	0.15
Mg^{++}	0.15	—	—	0.14
Na^{+}	0	—	—	0.14
$SO_4^{=}$	0.722	—	—	0.42
$SO_3^{=}$	0	—	—	0
HSO_3^{-}	0	—	—	0
Cl^{-}	0.05	—	—	0
$CO_3^{=}$	0.0	—	—	0.04
Solids Analysis (Wt%):				
$CaSO_3$	0	0	0	0
$CaSO_4$	0	0	0	0
$CaCO_3$	0	0	0	0
$Ca(OH)_2$	0	0	1	0
$MgSO_3$	0	0	1	0
$MgSO_4$	0	0	0	0
$MgCO_3$	0	0	0	0
$Mg(OH)_2$	0	0	0	0
Fly Ash	0	0	0	0

	16	17	18	21	22	23	24
LOOP STEAM							
Location	Absorber Outlet	Thickener Underflow	Filter Cake	Scrubber Feed Water	Flue Gas Exit	Dry Fly Ash	Lime Slurry
Flow Rate - Lbs/Hr or Gal/Min	1400	—	1400	17	1241	2.0	17
Composition:							
Σ Insoluble Solids	0	0	0.2-0.5	0.0-0.01	0	0.01	0.01
Liquid Analysis (M):							
Ca^{++}	0.45	—	0.1	—	0	0.01	—
Mg^{++}	0.15	—	0.15	—	0	0.01	—
Na^{+}	0	—	0	—	0	0	—
$SO_4^{=}$	0.722	—	0.34	—	0	0.34	—
$SO_3^{=}$	0	—	0	—	0	0.01	—
HSO_3^{-}	0	—	0	—	0	0	—
Cl^{-}	0.05	—	0.05	—	0	0.05	—
$CO_3^{=}$	0.0	—	0.04	—	0	0.02	—
Solids Analysis (Wt%):							
$CaSO_3$	0	0	0	7.32	—	7.34	1
$CaSO_4$	0	0	0	—	—	81.33	0
$CaCO_3$	0	0	0	—	—	0.34	0
$Ca(OH)_2$	0	0	1	4.13	—	1.69	7
$MgSO_3$	0	0	1	0.08	—	0.83	0
$MgSO_4$	0	0	0	—	—	—	0
$MgCO_3$	0	0	0	—	—	—	0
$Mg(OH)_2$	0	0	0	—	—	—	0
Fly Ash	0	0	0	—	—	—	0

[1] Balance Gas Make Up: 1-10 ppm SO_2 in Flue Gas

[2] Flow in Lbs/Hr, Gallons, or Cubic/Hr

[3] See 1% Water Within Filter Cake

( ) — Designates an Earlier Average

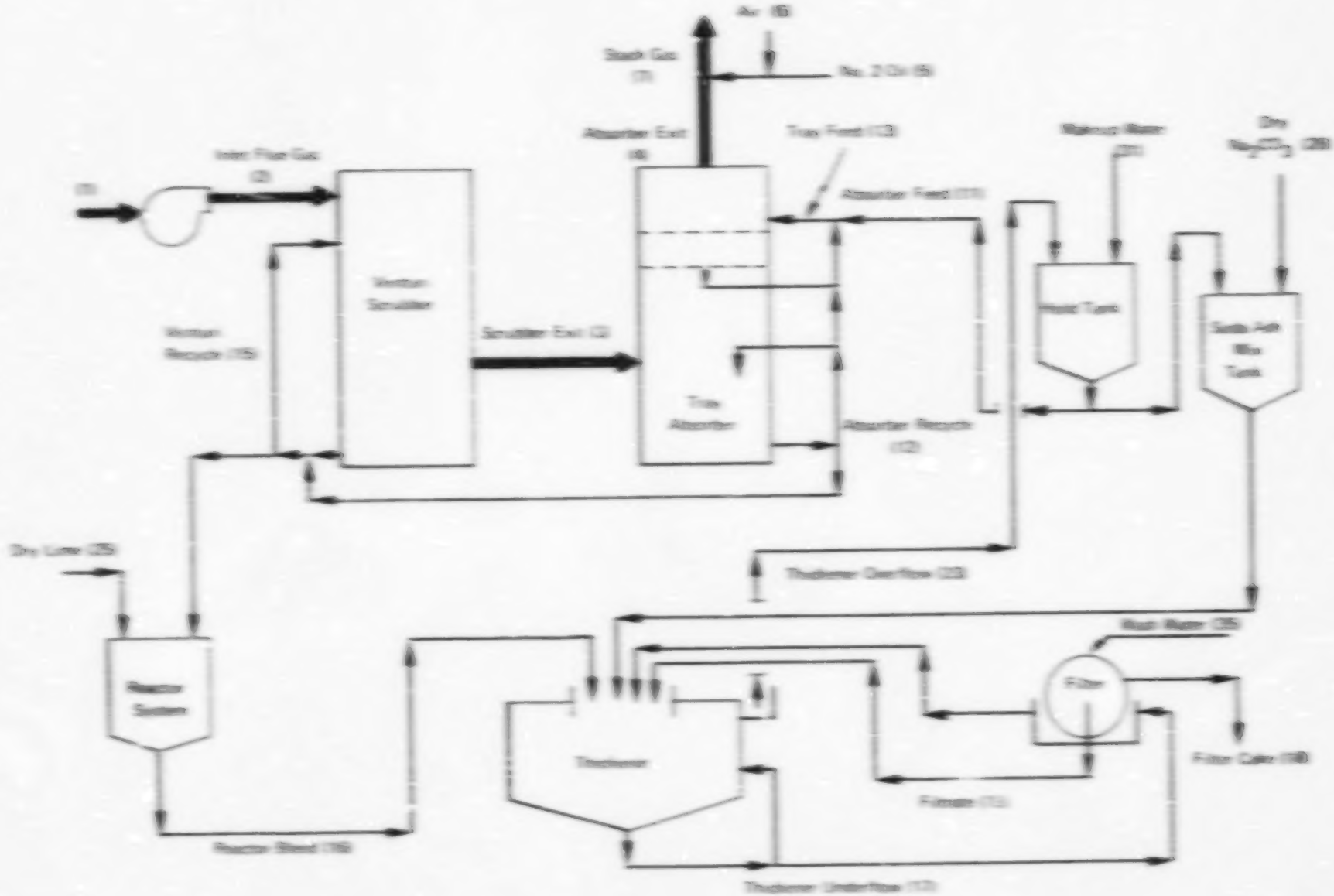

FIGURE D-3 SYSTEM CONFIGURATION--MAY 12, 1976 (PERIOD 3)
JUNE 22, 1976 (PERIOD 3)
JUNE 29, 1976 (PERIOD 3)

TABLE D-4

STEAM COMPOSITION, JUNE 27, 1976 - (TRIAL 3)

	1	2	3	4
Location	Inlet Gas	Scrubber Exit	Absorber Exit	Stack Gas
Flow Rate, lb/hr	71,500	—	—	—
Temperature, °F	300-320	134	120	120[a]
O2, vol%	2.6-3.8	—	—	7.1 avg.
CO2, vol%	(2%)	—	—	(<1)
H2O, vol%	(<1)	—	—	—
Particulate Loading, gr/scf dry	(<0.03)	—	—	(<0.02)
Pressure Drop, "WG		10.77	1.44	

	5	6	7	8	9	10	11	12	13	14	15
Location	Absorber Feed	Absorber Recycle	Tray Feed	Scrubber Recycle	Reactor Slurry	Thickener Underflow	Filter Cake	Thickener Overflow	Mix Tank Slurry	Mix Tank Water	Mix Tank Lime
Flow Rate, lb/hr or Stoichiometry	140	12,000	270	1200	1[b]	140	2000	1[b]	1777	0.5	0.0447
Composition:											
% Stoichiometric Excess	0	0	0	41.2	2.5+3	—	0	41.2	—	—	—
Liquid Analysis:											
pH	12.18	—	—	7.11	12.18	—	9	12.19	9	—	—
Ca^{++}	0.125	—	—	0.132	8.25_3	—	0	0.125	0	—	—
Mg^{++}	0	—	—	0.132	—	—	0	—	—	—	—
SO_4^{--}	0.77	—	—	0.06	(0.77)	—	0	0.79	—	—	—
SO_3^{--}	—	—	—	—	0.05_3	—	0	0.02	—	—	—
HCO_3^-	(<1)	—	—	—	—	—	0	—	—	—	—
Cl-	0.05_3	—	—	—	0.04	—	0	0.05_3	—	—	—
Ca++	(0.13+)	—	—	0.13%	(0.13+)	—	0	0.79	—	—	—
Solids Analysis:											
CaO	0	0	0	0	—	—	7.48	—	(100.0_3)	—	—
$CaSO_3$	0	0	0	0	—	—	0.25	—	(0.1_3)	—	—
$CaSO_4$	0	0	0	0	—	—	0.37	—	—	—	—
$CaCO_3$	0	0	0	0	—	—	1.26	—	—	—	—
$Mg(OH)_2$	0	0	0	0	—	—	0.77	—	—	—	—
Fly Ash	0	0	0	0	—	—	—	—	—	0.45	—
Ca(OH)2	0	0	0	0	—	—	(0.1_3)	—	(0.1)	—	—
Cl-	0	0	0	0	—	—	0.05_3	—	—	—	—
Ca++ Solid Equivalents	0	0	0	0	—	—	0.25	—	—	—	—

[a] Estimated

[b] — Flow in Liquid Equivalents or Stoichiometry

[c] Calculated on Dry Basis

(<1) — Estimated or Trivial Amounts

TABLE [illegible]

STEAM COMPOSITION, JUNE 25, 1975 - [illegible]

APPENDIX E

SOLUTION COMPOSITION/pH CORRELATIONS

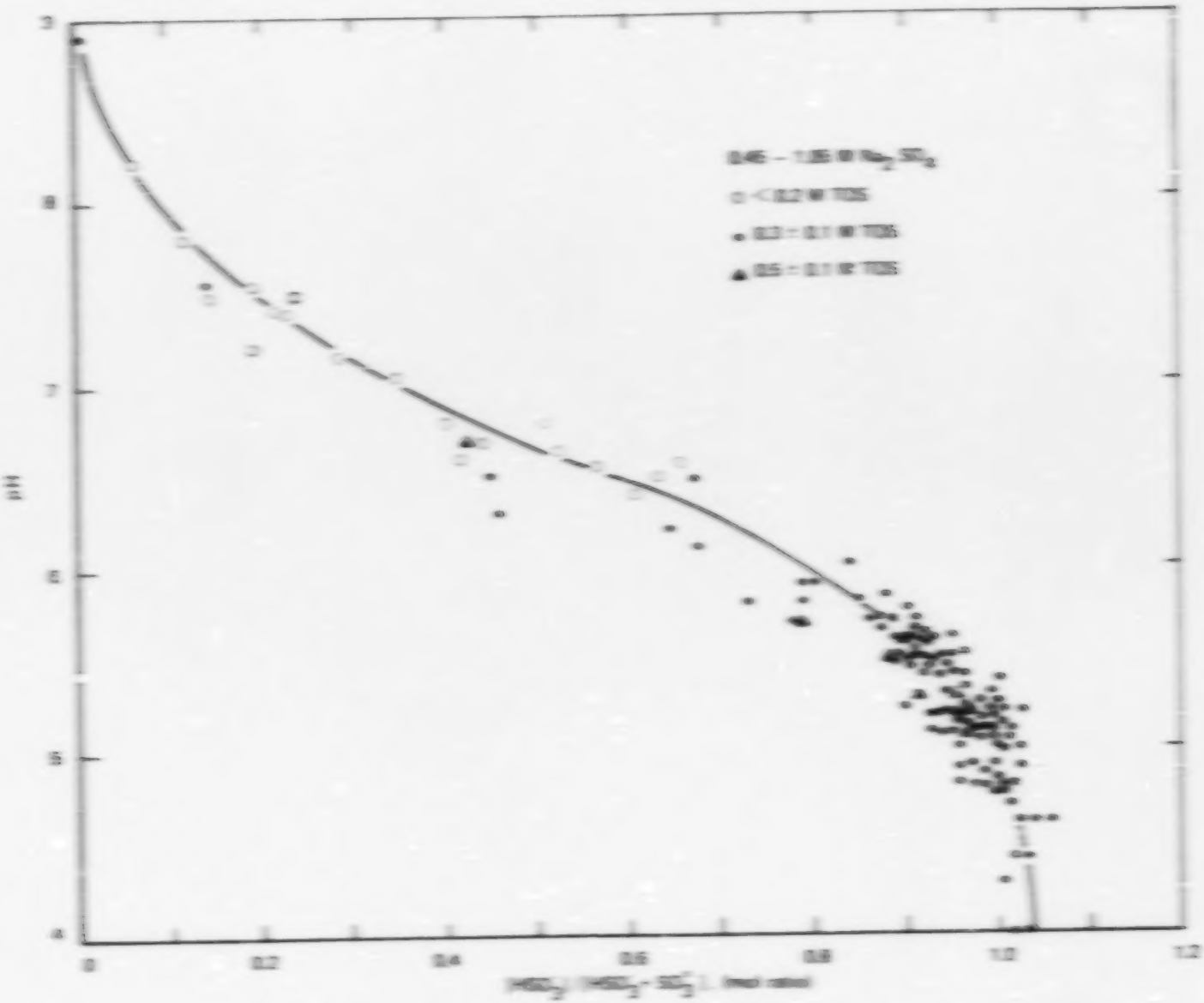

FIGURE 6-4

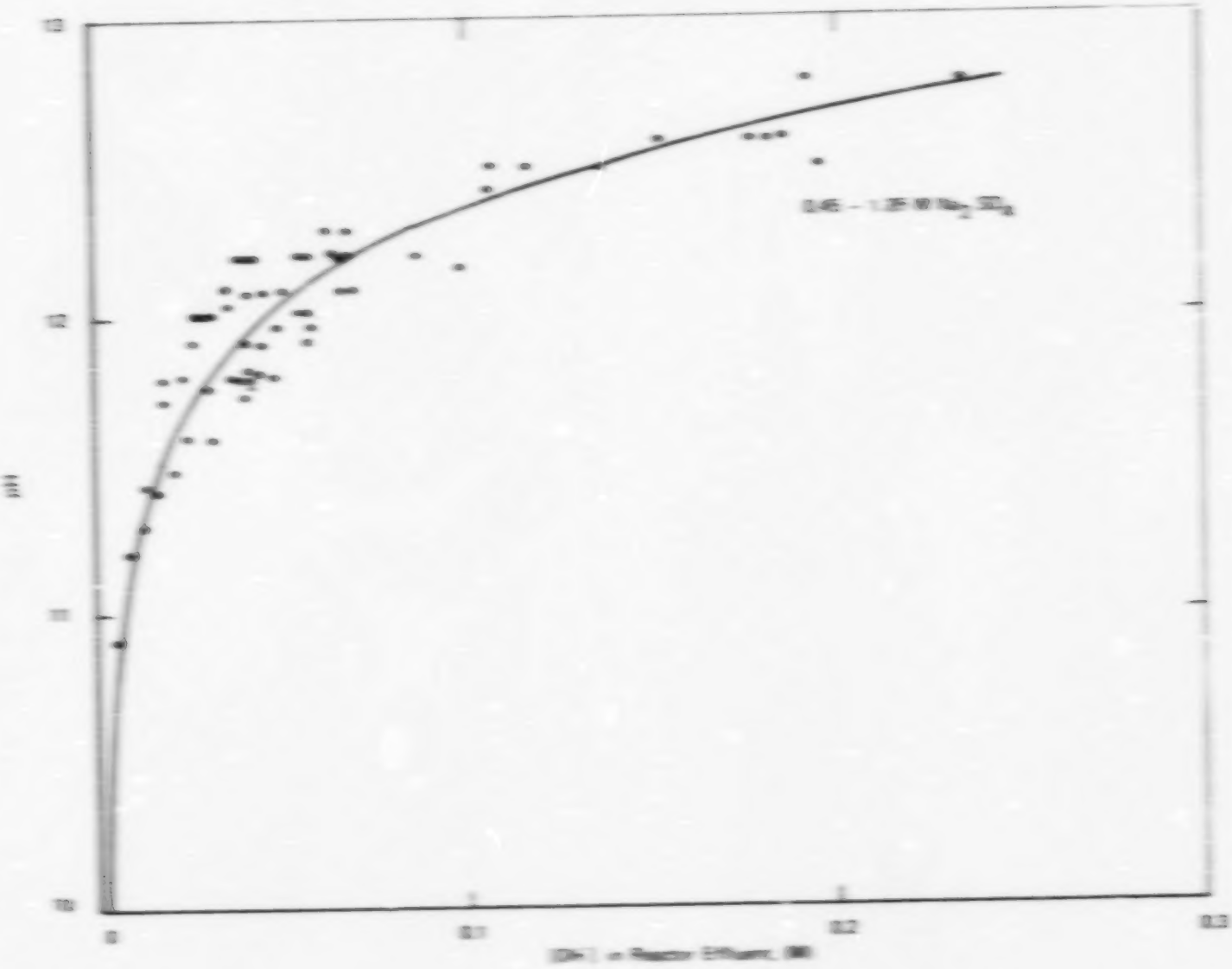

FIGURE 5-2 pH VS. [OH⁻] IN ABSENCE OF CARBONATE – SCHOLZ PLANT REACTOR EFFLUENT

APPENDIX F

SCRUBBER SYSTEM EFFICIENCY ESTIMATES

Estimates of scrubber stage efficiencies have been made based upon operating data obtained on the prototype system during stable load testing in Periods 2 (medium sulfur coal) and 3 (high sulfur coal). During these periods the venturi and absorber (with two trays) were operated in series. The system operating data used in calculating the stage efficiencies are summarized in Table F-1. Vapor-liquid equilibria data for SO_2 above sodium solutions were calculated from the equations of Johnstone[5]:

$$P_{SO_2}\ (mm\ Hg) = H\left[\frac{(2S - C)^2}{C - S}\right] \qquad (F\text{-}1)$$

where, $\log H = 4.319 - 1987/T(^\circ K)$; (F-2)

S = mols dissolved SO_2/100 mols of water; and

C = mols active sodium/100 mols of water

The method used in estimating the stage efficiencies is illustrated in Figures F-1 and F-2. The passing stream composition points were first located on plot of SO_2 gas composition versus S/C. The passing streams correspond to (inlet SO_2 concentration, venturi bleed liquor composition) and (outlet SO_2 concentration, estimated tray feed liquor composition). The tray feed liquor was not sampled so the composition was estimated based upon known rates of the regenerated liquor flow to the scrubber system and tray tower recycle flow; the composition of the regenerated liquor; and the pH of the recycle liquor. The tray tower and venturi operating lines were then located. As can be seen in Figures F-1 and F-2, the estimated stage efficiencies are relatively insensitive to variations in the composition of the tray feed liquor because of the steep slope of the tray tower operating line and the low vapor pressures of SO_2 for liquor compositions in this range. Thus relatively large errors in estimating the tray feed liquor have almost no impact on estimated stage efficiencies.

The stage efficiencies were then estimated based upon the assumption of equal efficiencies for all stages by the iterative procedure of assuming the stage efficiency until the passing stream composition points were matched. This procedure yields an average efficiency of 77% for each stage. Actually, the venturi would be expected to have a stage efficiency much lower than that of the trays; however, the data are not sufficient to allow a reasonable differentiation of the different stages. More operating data over a wide range of pH's and SO_2 concentrations, or internal scrubber stream compositions would be required to accurately define the different stage efficiencies.

TABLE F-1

STAGE EFFICIENCIES

DATE	11/17/75	5/28/76
SO_2 CONCENTRATIONS, (ppm)		
Inlet	1,160	2,400
Outlet	27	40
GAS FLOW, (scfm, dry)	43,600	44,500
SAT'D GAS TEMPERATURE, (°F)	130	130
TRAY TOWER OPERATION		
Regenerated Liquor to Scrubber System, (gpm)	120	160
Total Tray Feed, (gpm)	320	270
Tower Pressure Drop, (inches of water)[a]	6	---
VENTURI OPERATION		
Recycle Flow, (gpm)	1,440	1,290
Venturi Pressure Drop, (inches of water)	6	5.5
LIQUOR COMPOSITIONS, (M)		
Regenerated Liquor		
$[SO_3^=]$	0.124	0.110
$[OH^-]$	0.046	0.143
$[CO_3^=]$	0.011	0.016
$[Cl^-]$	0.035	-
$[SO_4^=]$	0.082	-
Venturi Bleed		
$[SO_3^=]$	0.030	0.062
$[HSO_3^-]$	0.250	0.236
$[Cl^-]$	-	-
$[SO_4^=]$	0.94	0.75

[a]Pressure drop includes two trays, demister and intermediate ducting.

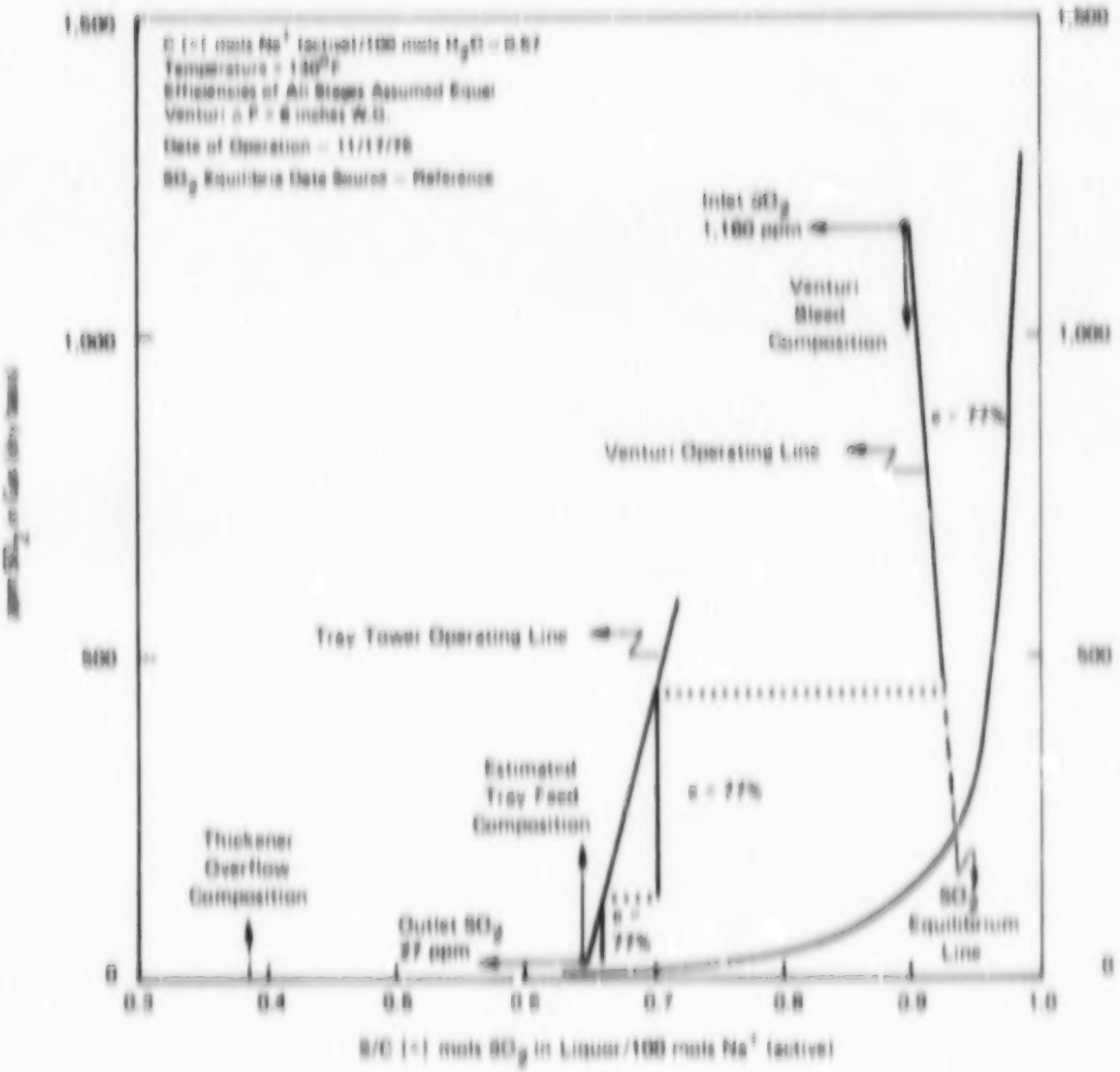

FIGURE F-1 STAGE EFFICIENCY ESTIMATES FOR MEDIUM SULFUR COAL OPERATION

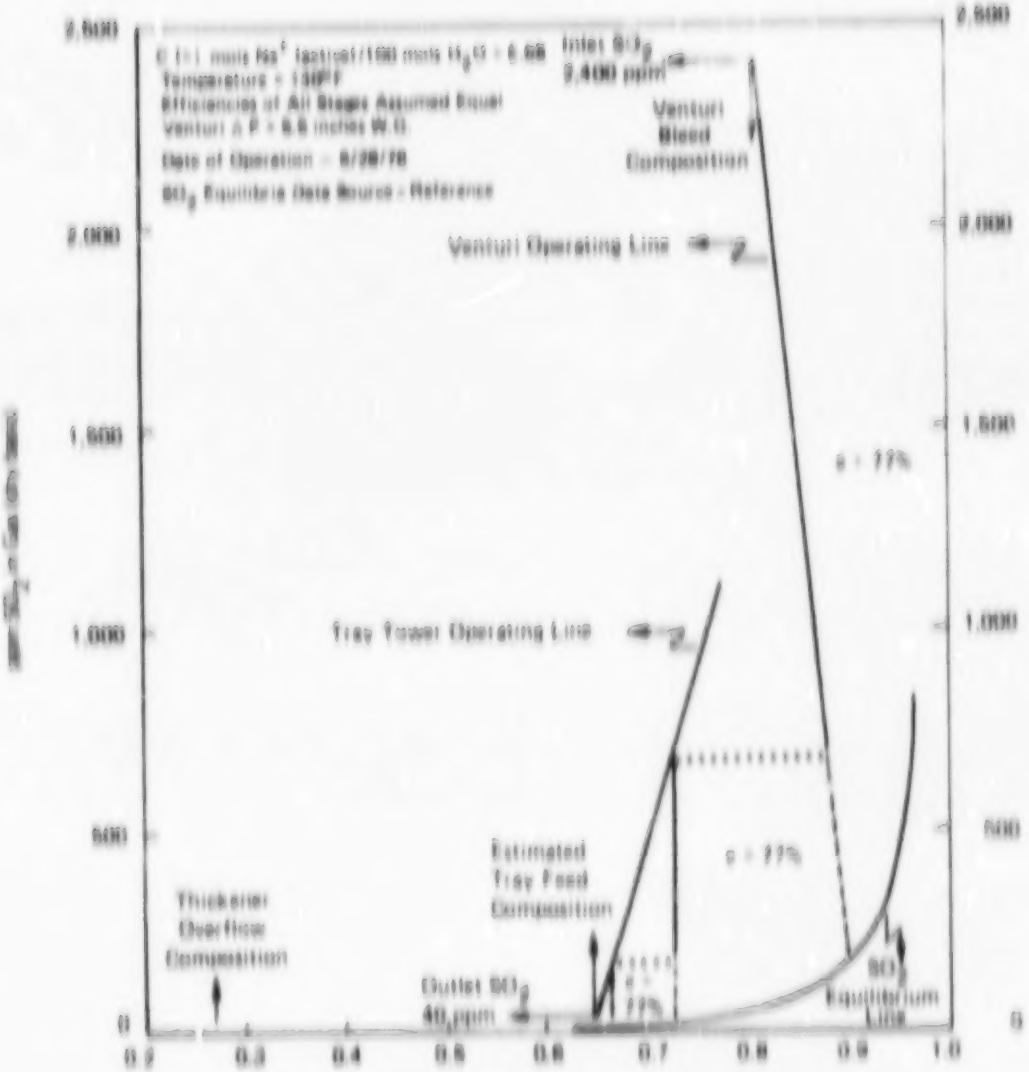

FIGURE F-3 STAGE EFFICIENCY ESTIMATES FOR HIGH SULFUR OPERATION (PERIOD 3)

APPENDIX G

EQUIPMENT PROBLEMS

[illegible]

Section	Position	Period of acceptance	Action	Resolution
[illegible]	MECHANICAL:			
	• [illegible]	[illegible]	[illegible]	[illegible]
	• [illegible]	[illegible]	[illegible]	[illegible]
	• [illegible]	[illegible]	[illegible]	[illegible]
	• [illegible]	[illegible]	[illegible]	[illegible]
	• [illegible]	[illegible]	[illegible]	[illegible]
	• [illegible]	[illegible]	[illegible]	[illegible]
	• [illegible]	[illegible]	[illegible]	[illegible]
	• [illegible]	[illegible]	[illegible]	[illegible]
	• [illegible]	[illegible]	[illegible]	[illegible]
	• [illegible]	[illegible]	[illegible]	[illegible]
	[illegible]			
	• [illegible]	[illegible]	[illegible]	[illegible]
	• [illegible]	[illegible]	[illegible]	[illegible]
	• [illegible]	[illegible]	[illegible]	[illegible]

[illegible]

[illegible]

[illegible]	Problem	Interval of Occurrence	Action	Resolution
[illegible]	• Loss of vacuum due to cracks in internal fiberglass insulation tubes in filler	[illegible]	Tested cracks—new caulking strip helped stress on interfaces when installing liners, thus overhauled prior to Period 3	Corrected
	• Shoulder-cracking of fiberglass bucket arm on tool agitator	1	Reinforced [illegible] (Period 3)	Corrected
	• Insufficient agitation in filler hub to suspend wash-like particles and grit	[illegible]	Increased[illegible] wash hub-agitator contact per period to Period 3	Corrected
	• Plugging of thickener underflow lines	1	Installed flexible lines and new high-flushing provisions (Period 3)	Corrected
	• Obsolescence of portions of lining in thickener and thickener hold tank	1	Tests and replace lining under warranty (Period 3)	Corrected
	• Failure of thickener rake motor overload control	2	Replaced (Period 3)	Corrected
	[illegible]			
	• Poor reliability of flocculator level control transmitter on thickener hold tank	[illegible]	Replaced with features (Period 3)	Corrected
[illegible]	[illegible]			
	• Clogging of dry feeder gate with lumps of soda ash	[illegible]	Replaced head control to allow higher gate position (Period 3)	Improved but still clogged occasionally
	• Failure of circuitry in heat tracing on piping	2	Replaced (Period 3)	Corrected
	[illegible]			
	• Poor reliability of level control system for soda ash liquor	[illegible]	Redesigned control/operating procedure (Period 3)	Corrected
[illegible]	[illegible]			
	• Water hammer damage to pump wash water header	2	Replaced, also adjusted operating procedure (Period 3)	—